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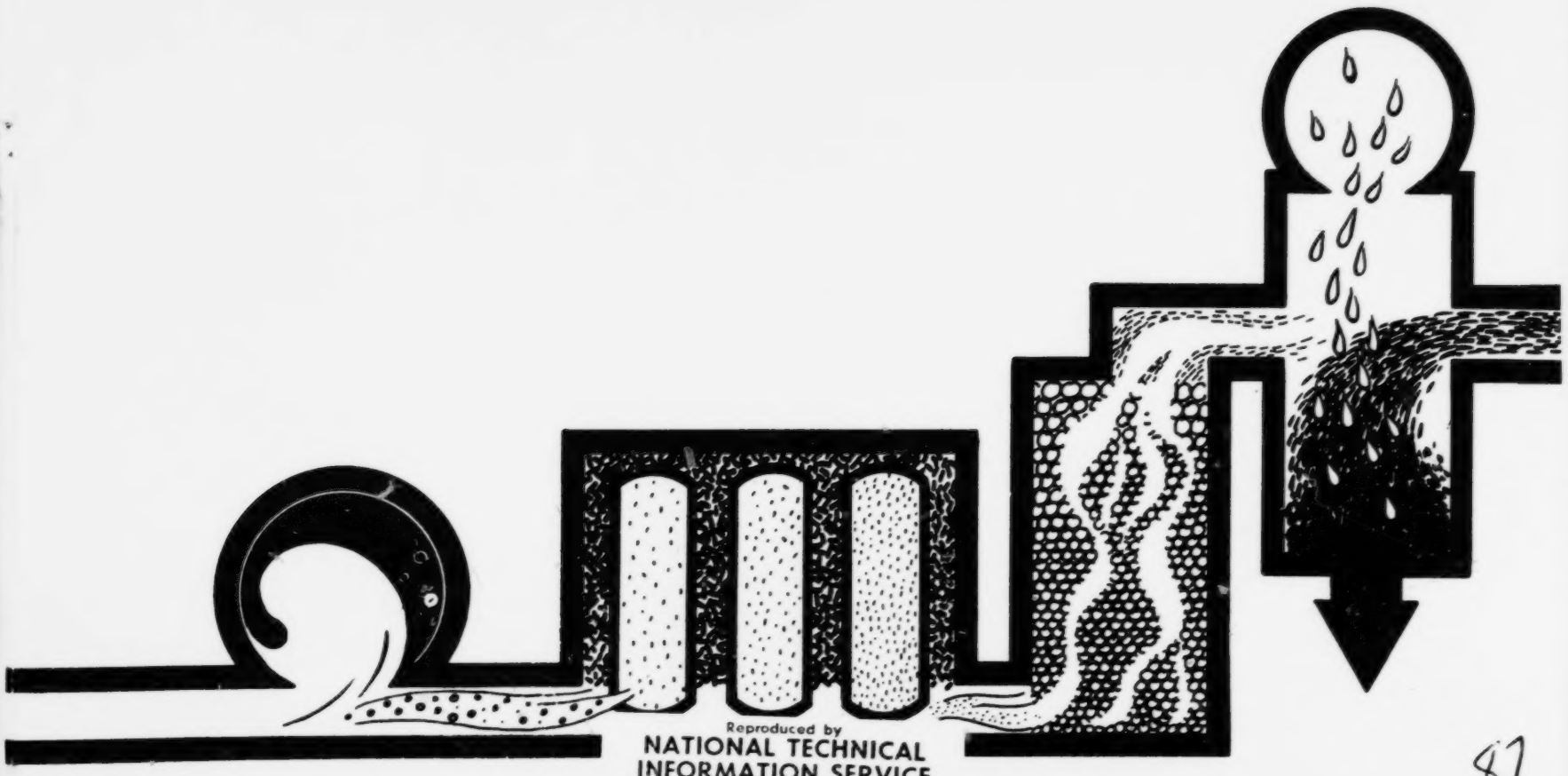
KINETICS AND MECHANISM OF PRECIPITATION AND NATURE OF THE PRECIPITATE OBTAINED IN PHOSPHATE REMOVAL FROM WASTEWATER USING ALUMINUM (III) AND IRON (III) SALTS



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27 Abstract

An investigation was conducted of the rate, mechanism and stoichiometry of phosphate precipitation with aluminum and ferric salts from pure phosphate solutions and secondary effluent. These studies showed that the reactions of orthophosphate ion with both Al(III) and Fe(III) are completed in less than 1 second. The effects of pH, reactant concentration, and reagent aging on the efficiency of phosphate removal were evaluated in batch precipitation experiments. The pH of optimum orthophosphate precipitation was found to be close to 6.0 for Al(III) and in the vicinity of 3.5 to 4.0 for Fe(III). With an initial orthophosphate concentration of 12 mg/l P, maximum phosphate removal was about 82% with Fe(III) and about 78% with Al(III) at a 1:1 molar ratio increasing to over 99% for both cations at a 2:1 ratio. At constant pH, with both Fe(III) and Al(III) up to about a 1:1 molar ratio, orthophosphate removal was directly proportional to amount of added cation, indicating occurrence of a chemical reaction. Dilute solutions of Fe(III) were found to undergo extensive hydrolysis on aging with a resultant loss of capacity to precipitate phosphate. The removal of condensed phosphates by precipitation with aluminum and iron salts was found to be strongly dependent on pH and the reactant concentration ratio. Precipitates obtained in the reaction of orthophosphate with aluminum and ferric salts were examined by X-ray diffraction analysis after drying and heating to 104°C and to 600°C. Both precipates remained amorphous, except that ferric phosphate was identified after ignition at 600°C. (Selby-Texas)

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KINETICS AND MECHANISM OF PRECIPITATION AND NATURE OF THE PRECIPITATE OBTAINED IN PHOSPHATE REMOVAL FROM WASTEWATER USING ALUMINUM(III) AND IRON(III) SALTS

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ABSTRACT

Atomics International has conducted an investigation of the rate, mechanism and stoichiometry of phosphate precipitation with aluminum and ferric salts from pure phosphate solutions and secondary effluent. Reaction rate studies were conducted in a specially designed apparatus.

These studies showed that the reactions of the orthophosphate ion with both Al(III) and Fe(III) are completed in less than 1 sec. Lowering of the reaction temperature from ambient to 5°C did not result in any measurable change in the rate or extent of phosphate removal. In all cases examined, phosphate removal from solution was accompanied by complete precipitation of excess Al(III) and Fe(III) by hydrolysis reactions.

The effects of pH, reactant concentration, and reagent aging on the efficiency of phosphate removal were evaluated in batch precipitation experiments. The pH of optimum orthophosphate precipitation was found to be close to 6.0 for Al(III) and in the vicinity of 3.5 to 4.0 for Fe(III).

With an initial orthophosphate concentration of 12 mg/ℓ P, maximum phosphate removal was about 82% with Fe(III) and about 78% with Al(III) at a 1:1 molar ratio increasing to over 99% for both cations at a 2:1 ratio. At and near the optimum pH, large settleable flocs formed; just outside this range, colloidal suspensions were formed.

At constant pH, with both Fe(III) and Al(III) up to about a 1:1 molar ratio, orthophosphate removal was directly proportional to amount of added cation, indicating occurrence of a chemical reaction. Addition of excessive quantities of Al(III) and Fe(III) to an orthophosphate solution resulted in an impairment of precipitate settleability and often caused dispersion of the precipitate as colloidal particles.

Dilute solutions of Fe(III) were found to undergo extensive hydrolysis on aging with a resultant loss of capacity to precipitate phosphate. No such change occurred with an Al(III) solution under similar conditions over a 2-month period.

The removal of condensed phosphates by precipitation with aluminum and iron salts was found to be strongly dependent on pH and the reactant concentration ratio. When a 2:1 cation-to-phosphate equivalence ratio was used with pyrophosphate and tripolyphosphate, maximum removal of phosphate was observed at pH levels close to 4 and 5 with Fe(III) and Al(III), respectively. Practically no phosphate was removed at pH levels $\pm$ 1 unit from those for maximum removal. At a 1:1 cation-to-phosphate reactant ratio, neither Al(III) nor Fe(III) could effect any removal of tripolyphosphate at several pH levels examined. As with orthophosphate precipitation, good correlations were found between the formation and settleability of the precipitates and the extent of phosphate removal.

Precipitates obtained in the reaction of orthophosphate with aluminum and ferric salts were examined by x-ray diffraction analysis after drying and heating to 104°C and to 600°C. Both precipitates remained amorphous, except that ferric phosphate was identified after ignition at 600°C. No conclusions could be drawn from data on weight loss on ignition.

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INTRODUCTION

Phosphorus and nitrogen compounds which are present in domestic wastewater in appreciable concentrations, are important nutrients. The discharge of large quantities of these nutrients into natural waters promotes the growth of algae and results in eutrophication of lakes and similar deterioration of water quality in receiving streams. In recent years, the large growth of population and the astonishing economic and industrial expansion which have been experienced in many areas of the world have placed a growing burden on available water resources and have generated an increasing need for abatement of water pollution and reclamation and reuse of wastewaters. Accordingly, considerable effort has been directed toward the development of economical methods to achieve a high degree of wastewater treatment and to effect a near complete removal of undesirable nutrients.

Although both nitrogen and phosphorus compounds are essential to the growth of algae, phosphorus is generally considered to be a more critical nutrient because, unlike nitrogen, it can only be supplied by influx of phosphorus-containing compounds entering the receiving body of water. In contrast, certain species of algae, particularly the nuisance blue-greens, are capable of satisfying their nitrogen demand by direct utilization of the atmospheric nitrogen.(1) Thus, control of eutrophication may best be achieved through control of phosphorus. For this reason, a major portion of the research efforts on the elimination of nutrients from wastewaters has been directed toward the development of economical methods for the removal of phosphates.

Phosphorus is usually present in the wastewater in the form of organic phosphorus, inorganic condensed phosphates, and orthophosphates. Most of the organically-bound phosphorus compounds in the wastewater are present as particulate organic matter and as bacterial cells. Very little is known about the dissolved organic phosphorus compounds which are the by-products of bacterial metabolism and cell lysis. Inorganic condensed phosphates such as tripolyphosphate and pyrophosphate originate mainly in household detergents. Orthophosphate is an end product of microbial degradation of phosphorus-containing organic compounds; orthophosphate is also excreted in urine, and is the product of enzymatic hydrolysis of condensed phosphates. Phosphorus in the orthophosphate form is most readily available for biological utilization. The concentrations of the various forms of phosphorus in domestic wastewater are subject to wide hourly and daily fluctuations. Wastewaters received at or discharged from different plants also contain varying concentrations of phosphates depending on the type of community served and the nature of the biological treatment process employed. Finstein and Hunter[2] studied phosphate concentration in three activated sludge and three trickling filter plants and found that in the influent to the biological treatment units inorganic condensed phosphates constituted 15 to 75% of the total phosphorus and that about 50% of the condensed phosphates were hydrolyzed to orthophosphate on their passage through the treatment plants.

To date, the most common methods of wastewater treatment involve biological oxidation. The microorganisms present in the wastewater degrade the complex organic molecules into simpler products thereby acquiring

energy and material for their growth and the synthesis of new cells. As the supply of the available food diminishes, the starving bacteria agglomerate into large flocs which are removed by settling. Although conventional biological treatment processes can result in a substantial reduction of the carbonaceous organic matter, only 20 to 40% of the phosphorus compounds initially present in the raw wastewater is converted into removable cell material due to the unique nutritional requirements of sewage bacteria. Accordingly, the effluents from most conventional biological treatment units still contain substantial quantities of phosphates (about 5 to 30 mg/ℓ P[2]) which have to be essentially completely removed if serious deterioration of water quality in the receiving streams is to be avoided. Phosphorus concentrations in excess of 0.01 mg/ℓ in natural waters have been shown to be conducive to the development of massive algae growth.[3]

Of the several methods available for the removal of phosphates, chemical precipitation using aluminum, ferric and calcium salts has received the widest attention. Despite considerable research, the basic chemistry of the phosphate reactions with the above cations, Al(III) and Fe(III) in particular, remains obscure; data reported in the literature have often been quite contradictory. To illustrate, Lea et al.[4] and Henriksen[5] presented results supporting the view that the removal of phosphate involves its adsorption on precipitating aluminum and ferric hydroxides. According to Stumm,[6] and Cole and Jackson,[7] however, the interaction of aluminum and iron with orthophosphates results in the formation of insoluble metal phosphates. Considerable disagreement also exist between various investigators on the kinetics and stoichiometry of cation-phosphate reactions, and

on the effect of various parameters such as pH and ionic concentrations on the efficiency of phosphate removal. Thus, Stumm[6] reported that under proper pH conditions and at low cation-to-phosphate ratios, the reaction of cations with orthophosphate is $M^{+3} + H_2PO_4^- = MPO_4 + 2H^+$, provided that sufficient time for the precipitation is allowed. In actual practice, however, even under optimum pH conditions, the quantities of metal salts required for complete precipitation of phosphates far exceed the stoichiometric requirements. Further, Lea et al.[4] reported that in the treatment of sewage plant effluent with alum, mixing or flocculation times in excess of 12 min resulted in a decrease in soluble phosphate removal. The reaction of aluminum and ferric salts with the polyphosphates have also been the subject of much controversy. Sawyer[1] reported that both aluminum and ferric salts are highly effective in removing all forms of phosphates. According to Stumm,[6] however, tripolyphosphates are not removable to any appreciable extent, by either Al(III) or Fe(III) due to the formation of soluble complexes such as $MP_3O_{10}^{-2}$.

Numerous discrepancies exist among the various reported values for the optimum pH for phosphate precipitation with Al(III) and Fe(III) salts. On the basis of certain solubility considerations and equilibrium data, the pH of minimum solubility for $AlPO_4$ and $FePO_4$ were calculated by Stumm[6] to be 6.3 and 5.3, respectively. Data reported by Henriksen,[5] however, indicate that the capacity of ferric sulphate to precipitate orthophosphate is greatest at a pH close to 4.0 and that the pH range for optimum removal of phosphate is broadened by an increase in the amount of added metal cation. The literature does not appear to contain any data on the effect of pH on the removal of polyphosphates by precipitation.

In an attempt to resolve some of the uncertainties and contradictions which have been briefly discussed above, a parametric study has been undertaken of the kinetics and stoichiometry of precipitation, and the nature of the precipitate obtained in phosphate removal using ferric and aluminum salts. While most of the precipitation studies were made on pure solutions of ortho-, pyro-, and tripoly-phosphates, actual wastewater effluent from a biological sewage treatment plant was used in some of the experiments. The specific objectives of the study which is described in this report have been to define: (a) the kinetics and mechanism of cation-phosphate reactions; (b) the stoichiometry of phosphate removal as a function of pH and reactant concentrations, and (c) the physical and chemical nature of the precipitates formed.

EXPERIMENTAL

This section describes the materials, apparatus, and procedures used generally during the course of the investigation. Special methods and modifications are described with the results where appropriate.

Materials

Reagent grade sodium monohydrogen (ortho-) phosphate, tetrasodium pyrophosphate, sodium tripolyphosphate, ferric nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] and aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$] were used to prepare pure test solutions. All Al(III) and Fe(III) solutions were prepared fresh daily. After the rapid rate of Fe(III) hydrolysis became recognized as a factor in these studies, the test Fe(III) solutions were prepared just prior to the experiments. Adjustment of pH was made using reagent grade HCl or NaOH. All

other reagents used were the purest grade available. Double distilled water was used to prepare reagent solutions.

The orthophosphate solution used in most experiments contained 12 mg/ℓ P Na_2HPO_4 (11.58×10^{-4} equivalents/ℓ PO_4^{-3} or 3.86×10^{-4} M). This concentration was selected as representative of that to be encountered in a high phosphate secondary effluent. An 18 mg/ℓ P solution of tetrasodium pyrophosphate (11.58×10^{-4} equivalents/ℓ $P_2O_7^{-4}$) and 21.6 mg/ℓ P solution of sodium tripolyphosphate (11.58×10^{-4} equivalents/ℓ $P_3O_{10}^{-5}$) were used in the experiments with condensed phosphates.

The wastewater (secondary effluent) used in these studies was obtained from the Tapia Park Treatment Plant of the Las Virgenes Municipal Water District in Calabasas, California. This treatment plant is a small (~ 2 mgd) activated sludge plant which serves a primarily residential community. It employs an aerobic sludge digestion process with the supernatant liquor returned to the head of treatment plant. The small amount of large bacterial flocs which were present in the effluent was removed by prior filtration through coarse filter paper.

The following is a partial analysis of the filtered effluent used in the phosphate precipitation experiments with Al(III):

pH	7.8
Temperature (°C)	17.5
Conductivity (at 17.5°C)(mmhos/cm)	2.17
Turbidity (JTU)	0.73
Orthophosphate (mg/ℓ P)	7.75
Total phosphate (mg/ℓ P)	7.75
Polyphosphate (by difference)(mg/ℓ)	0

The effluent used in kinetics experiments with Fe(III) and Al(III), and in other experiments with Fe(III), was analyzed for phosphate content only; it contained 9.0 mg/ℓ P orthophosphate.

Apparatus

Commercial Items

All "jar test" precipitation experiments were conducted using Phipps and Bird six place stirrers (Phipps and Bird, Inc., Richmond, Va.). The metal paddles supplied with the instruments were replaced with clear plastic paddles to avoid possible metallic contamination of the test solutions. Radiometer PHM 26 and PHM 28 pH meters (Radiometer Co., Copenhagen) and a Beckman Model 96 Zero-matic pH meter (Beckman Instrument Co., Fullerton, Calif.) were used for pH measurements. All conductivity determinations were made with Radiometer Model CDM2e conductivity meters (Radiometer Co., Copenhagen). The conductivity cell was modified by drilling numerous holes in the glass envelope to permit easier passage of the solution between the electrode surfaces. A Radiometer automatic titration control unit, type TTT 11 (Radiometer Co., Copenhagen) was used in conjunction with the Radiometer pH meters for the constant pH precipitation experiments. A Moseley Model 7100 B two pen strip chart recorder (Hewlett-Packard Co., Pasadena, Calif.) was used for recording pH and conductivity. All turbidity measurements were made with a Hach Laboratory Turbidimeter Model 2100 (Hach Chemical Co., Ames, Iowa). Except where otherwise noted, colorimetric analyses were made with a Bausch and Lomb Spectronic 20 Colorimeter/Spectrophotometer (Bausch and Lomb Co., Rochester, N.Y.). All x-ray diffraction analyses were made on a Norelco 50 KV Diffractometer (Norelco, New York, N.Y.).

Kinetics Apparatus

To obtain reliable data on the rates of the phosphate precipitation reactions, a special reaction kinetics apparatus, shown schematically in Figure 1, was designed and constructed. In this apparatus, provision was made for monitoring pH, and residual phosphate and cation concentrations under steady-state conditions. The metal salt and phosphate solutions flow by gravity from separate reservoirs into a 50 ml reaction flask where they are rapidly mixed with a magnetic stirrer. The mixture then flows through a long 16 mm I.D. tube, assembled from 4-ft Pyrex sections connected by short pieces of rubber hose with openings for sampling or insertion of a pH probe electrode. Samples of the flowing solution mixture are withdrawn through 450 mμ membrane filters in Millipore Swinnex-25 filter units (Millipore Corp., Bedford, Mass.) by vacuum filtration. The filtrates are analyzed for residual phosphate and metal ion content.

The mixing apparatus was shown to be effective by reacting a dilute solution of sodium hydroxide containing phenolphthalein indicator with a dilute HCl solution. No color was observed in the fluid leaving the mixing flask. Indeed, little, if any, color was observed beyond the point where the two streams entered the flask.

In the initial experiments, where the Swinnex-25 filter units were attached as supplied to the flow line, the membrane filter surface was separated from the flowing liquid by a volume of approximately 1 ml. With the very slow filtration rate obtained, the residence time of the liquid within the filter head could have been as long as 30 sec. To eliminate such a long residence time, the Swinnex-25 filter holders, with their inlet

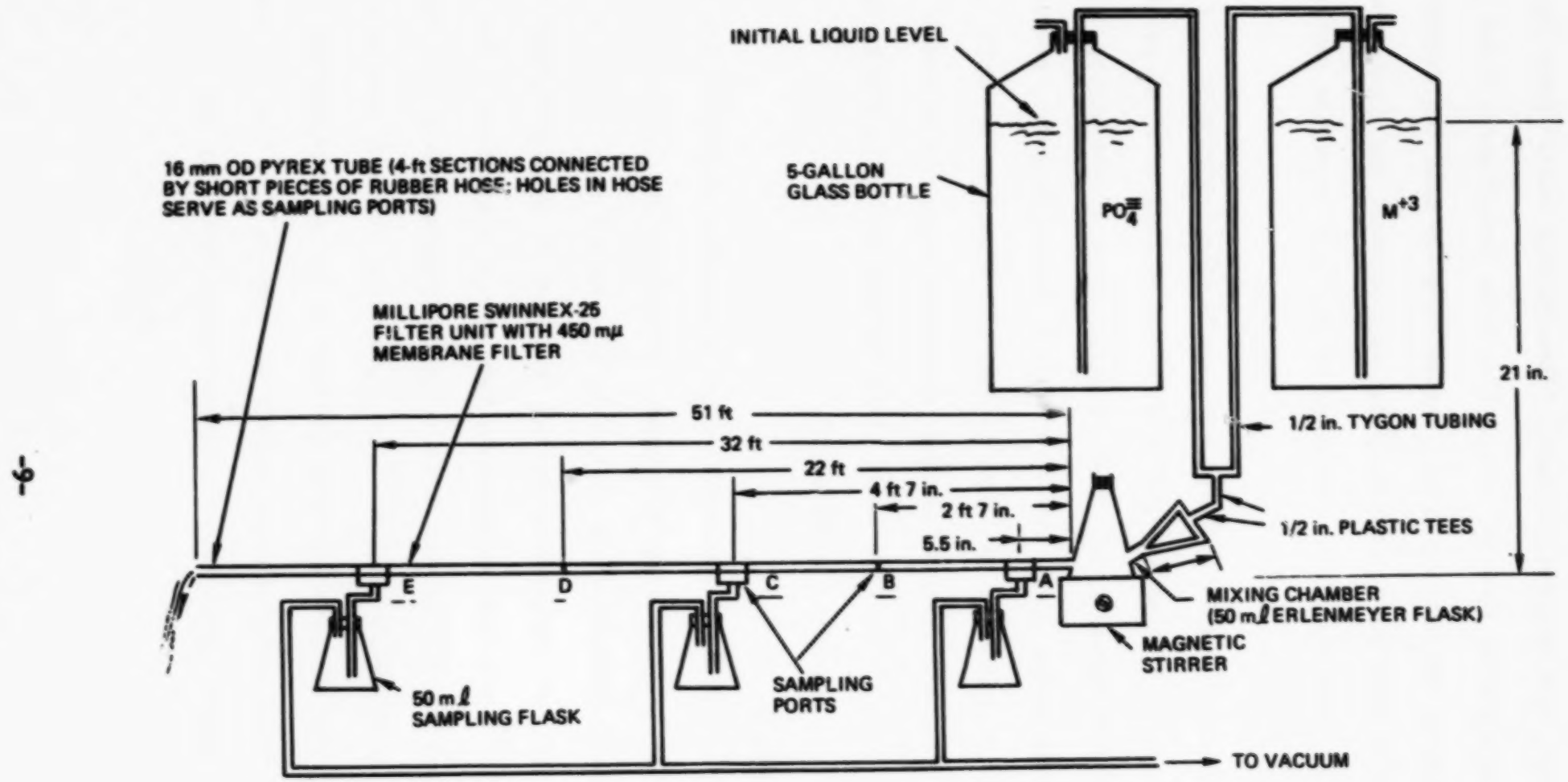

Figure 1. Schematic Diagram of the Reaction Kinetics Apparatus (Not Drawn to Scale)

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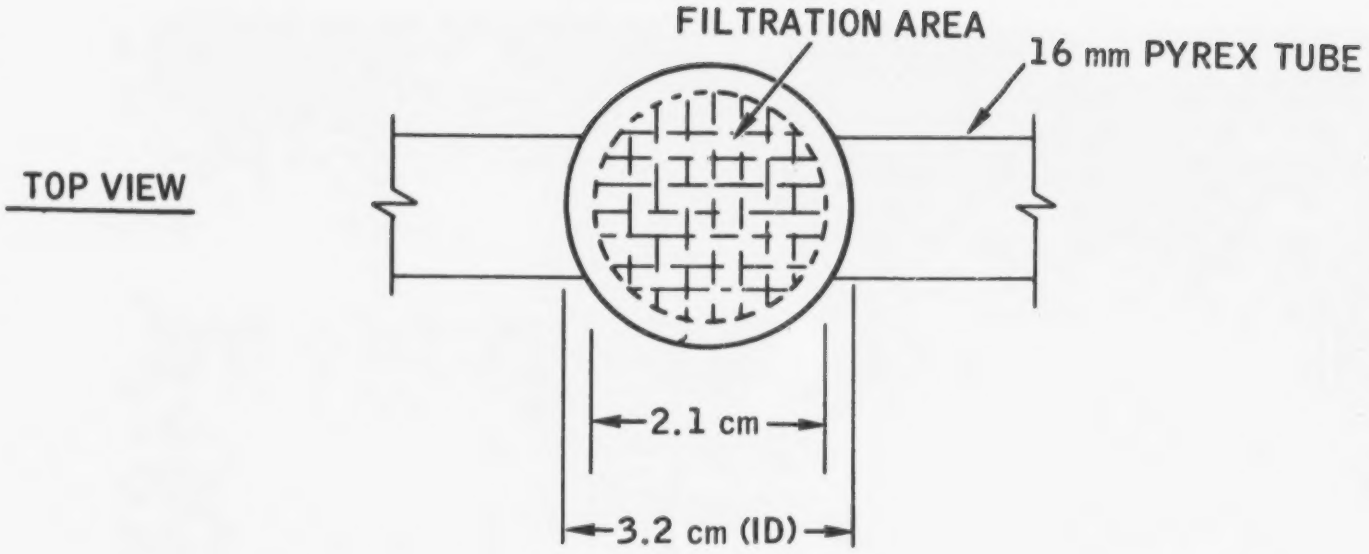
sections cut away, were attached to small "flow-through cells" (see Figure 2), which were placed directly in the flow line (see Figures 2 and 3). In this arrangement, the flowing liquid passes directly over the entire filtration area so that the filtrates collected represent the liquid phase prevailing at the sampling ports. The time of solution travel to each port is thus the true reaction time prior to filtration.

Most of the experiments with the reaction kinetics apparatus (Figure 1) were conducted with an average total solution flow of 65 ml per sec, yielding approximate total travel times from the start of the mixing to the three sampling ports, A, B, and C, of 1.3, 4.3, and 22.2 sec, respectively. In some experiments, the time of solution travel to the first port was reduced to less than 1 sec by further elevating the solution reservoirs and by shortening the flow line. A photograph of the apparatus in this arrangement is presented in Figure 3.

Analytical Procedures

The stannous chloride method described in Standard Methods[8] was used for all orthophosphate determinations. With the 2 cm light path employed, phosphate concentrations as low as 0.01 mg/ℓ P could be detected. The polyphosphates were analyzed by hydrolyzing them to orthophosphate by boiling with acid[8] and then determining them as orthophosphate. The benzene-isobutanol extraction modification of the stannous chloride method recommended in the Standard Methods[8] for obtaining increased sensitivity and avoidance of certain interferences was used in all orthophosphate determinations involving wastewater samples and samples from Fe(III) precipitation experiments. The ether extraction modification of the



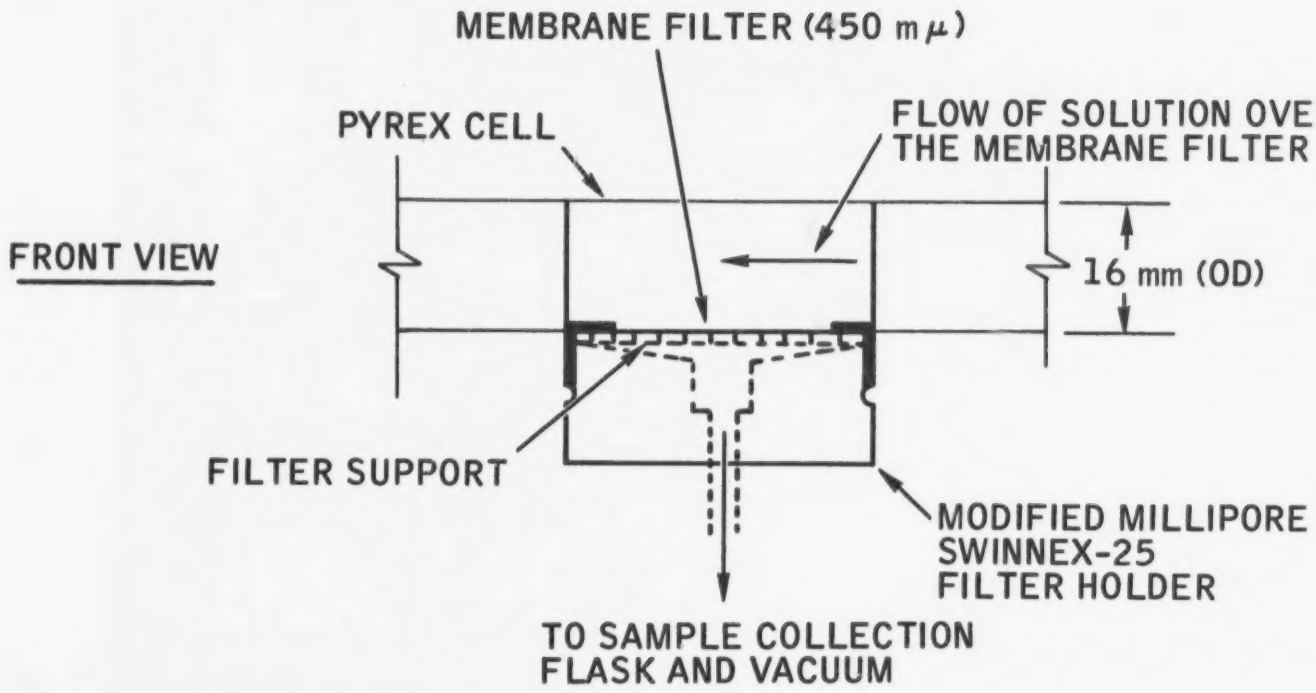


Figure 2. Schematic Diagram of the Flow-Through Sampling Port Used in the Reaction Kinetics Apparatus

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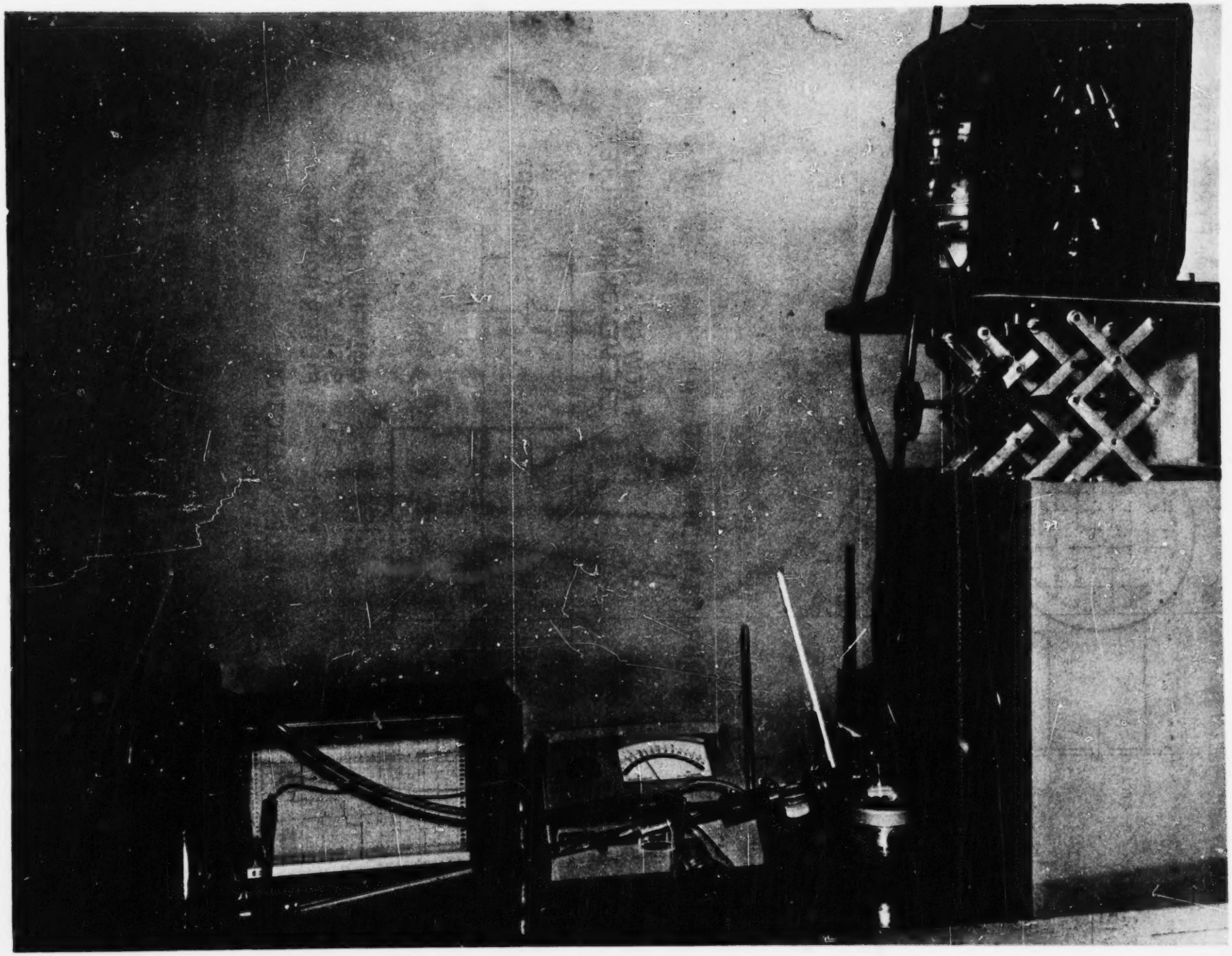

Figure 3. Reaction Kinetics Apparatus, Modified for Rapid Flow

orthophenanthroline method described in Standard Methods[8] was used in all iron determinations. With the 2 cm light path employed, as little as 0.2 mg/ℓ Fe could be detected by this method. In some cases, however, samples were concentrated several fold prior to extraction to increase the sensitivity of the method. All Al(III) analyses were made using the 8-hydroxyquinoline-chloroform extraction method described by Sandell.[9]

Experimental Procedures

Jar Test Experiments

Many of the studies were carried out in batch type ("jar test") experiments. The usual procedure in these tests was as follows. Five hundred ml of the test phosphate solution was placed in a 1 ℓ beaker, with pH electrodes and a conductivity cell. While stirring at 90 rpm, 5 ml of an aluminum or ferric nitrate solution of appropriate concentration (7.72×10^{-2} M, 3.86×10^{-2} M, or 1.93×10^{-2} M) was added to establish cation-to-phosphate molar ratios of 2:1, 1:1, or 0.5:1. After 2 min of rapid mixing at 90 rpm, the stirring rate was slowed to 20 rpm and mixing was continued at this rate for 10 min or more, followed by 20 min of quiescent settling. The settled samples were then filtered through Whatman #42 filter paper and the filtrates analyzed for residual phosphate and cation (Al or Fe) content. Prior to filtration, a portion of the sample supernatant was decanted into a turbidimeter test cell and its turbidity was determined.

In the experiments with condensed phosphates and secondary sewage effluent, and in some initial experiments with orthophosphate, all pH adjustments were made by prior addition of NaOH or HCl to the phosphate test

solution. In most orthophosphate precipitation experiments, a Radiometer automatic titrator was used to maintain constant pH through addition of NaOH while the aluminum or ferric salt solution (1-10 ml) was slowly added. All batch-type experiments were conducted at ambient temperature (25 $\pm$ 2°C).

Experiments with the Reaction Kinetics Apparatus

In the kinetics studies with the special apparatus described above, both pure solutions of orthophosphate and secondary effluent were used. The phosphate solution used contained 24 mg/ℓ Na_2HPO_4 (7.72×10^{-4} M) which upon mixing with the cation solution of the same molarity at nearly equal flow rate, yielded a final phosphate concentration of about 12 mg/ℓ P (3.96×10^{-4} M). Early reaction rate studies indicated that the capacity of a dilute solution of Fe(III) to precipitate phosphate is significantly reduced when the solution is aged. Accordingly, in later experiments both aluminum and ferric stock solutions were prepared fresh in concentrated form and were diluted to 18 ℓ immediately prior to start of each experiment. These kinetics experiments were completed within 10 min. The final solution pH in each experiment was maintained within the pH range (4-5.5 for Fe(III) and 5-7 for Al(III) for optimum phosphate precipitation and good floc formation by prior addition of NaOH to the phosphate solution.

The reaction kinetics experiment with secondary effluent and Al(III) was conducted at a final solution pH of 5.7-5.8, using an Al(III)/PO_4^{-3} molar ratio of 1:1; the corresponding Fe(III) experiment was conducted at a final solution pH of 5.2-5.3 using a 2:1 Fe(III)/PO_4^{-3} molar ratio.

Except for two experiments which were conducted at 5°C, all reaction rate studies were performed at ambient temperature (25 $\pm$ 2°C). The water used in preparing the test solutions for the 5°C experiments was precooled in a refrigerator.

In the majority of experiments, samples of solution mixture leaving the kinetics apparatus were collected and flocculated by slow (20 rpm) mixing. Following settling, the supernatants were filtered through 450 mμ membrane filters and the filtrates were analyzed.

Other Experiments

As mentioned previously, aging of a dilute solution of Fe(III) results in the loss of its effectiveness for phosphate removal. To investigate this aging more thoroughly and to compare it with the behavior of Al(III), a number of experiments were conducted in which the pH, conductivity and the orthophosphate removal capacity of dilute (7.72×10^{-4} M) solutions of aluminum and ferric nitrate salts were monitored over extended periods of time. These were done at room temperature (~ 25°C); the conductivity experiment on Fe(III) was thermostated in a water bath at 25°C. In the experiments with Fe(III), aliquots of the dilute stock iron solution were separately filtered through 100 mμ membrane filters at selected intervals following dilution and the filtrates were analyzed for residual Fe(III) content. In assessing the effect of aging on phosphate removal capacity, 250 ml portions of the stock aluminum or iron solutions (7.72×10^{-4} M) were added to 250 ml samples of a 24 mg/ℓ P (7.72×10^{-4} M) Na_2HPO_4 solution following various periods of aging. The pH of the solution mixture was then rapidly raised to the desired level (pH 5.0 for Fe and pH 6.0 for Al) and the standard jar test procedure for phosphate precipitation was followed.

To investigate the nature of the precipitates formed in phosphate removal using iron and aluminum salts, orthophosphate was precipitated from solutions of 12 mg/ℓ P Na_2HPO_4 (3.86×10^{-4} M) using a cation-to-orthophosphate molar ratio of 1:1. The precipitation experiments were conducted at

a pH of 6.0 for Al(III) and at a pH of 5.0 for Fe(III), using a Radiometer automatic titrator. Following the normal periods of flocculation and settling, the supernatant was decanted and the precipitate slurry was centrifuged and then washed into a pre-weighed Gooch crucible containing a glass fiber filter paper (No. 934-AH, Hurlbut Paper Co.). After filtration, the crucible was stored in a desiccator at room temperature until it reached a constant weight. It was then heated at 104°C for three 2-hr periods and ignited at 600°C for two consecutive 2-hr periods. The crucible was weighed at each step to determine the extent of weight loss. X-ray diffraction analyses were made on all dried and ignited precipitates to determine their chemical composition.

RESULTS AND DISCUSSION

Kinetics of Precipitation: Studies Using Jar Tests

The results of reaction rate studies obtained early in the investigation in batch precipitation experiments are presented in Table 1. In all cases where pH and conductivity were monitored during the precipitation experiment, the recorded changes in these variables were rapid and took place within 10 to 60 sec after the addition of the precipitating agent, with no measurable change in either pH or conductivity taking place after this period.

In one experiment using a 2:1 aluminum-to-orthophosphate molar ratio (final solution pH = 5.9), aliquots of solution were removed from the reaction beaker at 0.5, 1.0, 1.5, 4.0, 10.0, 22, and 32 min following addition of aluminum nitrate. Each aliquot was immediately and rapidly vacuum

TABLE 1

REACTION RATE STUDIES USING JAR TESTS

M(III)	Phosphate Solution Used	Cation-to-Phosphate Equivalence Ratio	Final Solution pH	Comments and Observations
Fe	12 mg/ℓ P Na_2HPO_4	1:1	4.15	pH monitored for 12 min; fell rapidly and remained constant at 4.15 after 30 sec of the addition of iron. Good floc formation was observed; residual phosphate concentration = 2.26 mg/ℓ P.
Fe	12 mg/ℓ P Na_2HPO_4	2:1	6.0	Conductivity monitored for 12 min; fell rapidly and remained constant after 20 sec of the addition of iron. The flocs developed did not settle very well; residual phosphate concentration = 0.60 mg/ℓ P.
Fe	18 mg/ℓ P $Na_4P_2O_7$	2:1	4.2	pH and conductivity were monitored for 12 min and found to reach constant values after 60 sec of the addition of iron; good floc formation observed; residual phosphate concentration = 0.46 mg/ℓ P.
Al	12 mg/ℓ P Na_2HPO_4	2:1	5.9	pH and conductivity were monitored for a period of 32 min and found to stay at constant levels after 30 and 60 sec of the addition of aluminum, respectively. The precipitate did not settle very well; residual phosphate concentration = 0.1 mg/ℓ P.
Al	12 mg/ℓ P Na_2HPO_4	2:1	6.3	pH and conductivity were monitored for a period of 32 min and found to remain at constant levels after 30 and 60 sec, respectively, following addition of aluminum salt solution.
Al	18 mg/ℓ P $Na_4P_2O_7$	2:1	5.0	pH and conductivity were monitored for a period of 32 min. A slight drop in pH (0.03 units) and a small rise in conductivity appeared to take place following the initial drops in pH and conductivity; good floc formation observed.

filtered through Whatman #42 filter paper and the filtrates were analyzed for residual phosphate content. The data indicated a drop in phosphate concentration from the initial 12 mg/ℓ P to 0.10 mg/ℓ in less than 60 sec following addition of aluminum nitrate. No further removal of phosphate was observed after this period, despite the very noticeable gradual growth and agglomeration of the precipitate flocs.

In an HCl-NaOH neutralization experiment, conducted under identical mixing conditions, the change in pH and conductivity with time followed a similar pattern to that observed in the phosphate precipitation experiments. Since this acid-base reaction is known to be instantaneous, the similarity of results indicated that cation-phosphate reaction which results in the lowering of pH and conductivity might indeed also be essentially instantaneous, and that the apparent time delay in attaining constant pH and conductivity levels could in fact be due to the time required for mixing to achieve uniform distribution of the added reagents.

Kinetics of Precipitation: Studies Using the Reaction Kinetics Apparatus

In the initial phosphate precipitation studies using the reaction kinetics apparatus, only the pH of the solution mixture leaving the reaction flask (see Figure 1) was monitored. In experiments with both Fe(III) and with Al(III), a constant value of pH was observed at all sampling ports. Judging from this constancy of pH, the reaction between phosphate and both aluminum and iron cations appears to be complete within 1.3 sec, i.e., the travel time to the first sampling port.

Data on the phosphate removal effected using the reaction kinetics apparatus are presented in Table 2. The data in Table 2 given by Experiment Nos. 1 through 8 were collected on samples removed and filtered through the

TABLE 2

DATA ON KINETICS OF M(III)-ORTHOPHOSPHATE REACTIONS[a,b]

Experiment No.	Cation M(III)	$M(III)/PO_4^{-3}$ Molar Ratio	pH[c]	Average Filtrate Analysis (450 mμ Millipore Filter)			Comments
				Turbidity (JTU)	Residual Phosphate (mg/ℓ P)	Residual M(III) (mg/ℓ)	
1	Fe	1:1	5.4-5.65	-[d]	8.44	-	e,f,g
2	Fe	1:1	4.5	0.08	8.43	0	e,f,g
3	Fe	1:1	4.85	0.13	7.24	0	e,f,g
4	Fe	2:1	4.5-4.6	-	1.91	-	e,f,g
5	Fe	2:1	4.8-5.3	-	1.92	0	e,f,g
6	Al	1:1	6.3-6.5	0.14	4.1	-	e,f,g
7	Al	2:1	6.8-7.2	0.3	1.39	-	e,f,g
8	Al	2:1	6.3-6.7	0.12	0.54	-	e,f,g
9	Fe	0.5:1	5.4-5.5	0.3	8.24	0	f,h,i
10	Fe	1:1	4.5-4.6	0.25	3.44	-	f,h,i
11	Fe	1:1	4.4	0.20	3.24	-	f,h,i
12	Fe	2:1	4.3-4.4	0.40	0.02	-	f,h,i
13	Al	1:1	6.2-6.4	-	4.58	0	f,h,i
14	Al	1:1	6.2-6.4	-	4.07	0	f,h,i,j
15	Fe	1:1	5.0-5.2	-	3.17	-	f,h,i,j
16	Al	1:1	6.3-6.4	-	4.12	-	h,i,k
17	Fe	1:1	4.0-4.1	-	3.76	0	h,i,k
18	Al	1:1	5.7-5.8	-	1.25	-	h,i,k,l
19	Fe	2:1	5.2-5.3	-	0.01	-	h,i,k,l

a. Initial PO_4^{-3} conc. in combined solution ≅ 12 mg/ℓ P except as noted
b. Reaction temperature ≅ 25°C except as noted
c. pH monitored at Port B (see Fig. 1)
d. Dash indicates measurement not made
e. Aged cation salt solution used
f. Combined solution flow ≅ 65 ml/sec
g. Swinnex filter holders used as received; residence time may be ~ 30 sec
h. Freshly prepared cation salt solution used
i. Modified Swinnex filter holders used; solution filtered directly
j. Reaction temperature ≅ 5°C
k. Combined solution flow ≅ 110 ml/sec
l. PO_4^{-3} conc. = 9.0 mg/ℓ P in secondary effluent; ≅ 4.5 mg/ℓ P in combined solution

Millipore Swinnex-25 filter units directly attached to the flow line. As described above in the section, "Kinetics Apparatus", with this arrangement the actual time before filtration might be considerably longer than the time of solution travel to the several sampling ports. These data are nevertheless included in this report, since they represent results with "aged" (hydrolyzed) cations. Also, these experiments with Al(III) cover a wider range of molar ratio than do those done with the modified filtration unit.

The data on phosphate removal collected using the modified sampling cells described above in the section "Kinetics Apparatus" are presented by Experiment Nos. 9 through 17. The aluminum and ferric salt solutions used in these later experiments were prepared immediately before the start of each experiment which was completed within 10 min of the preparation of these dilute solutions. Comparison of these residual phosphate concentrations with those obtained using aged ferric and aluminum salt solutions (Experiment Nos. 1 through 8) indicates that while dilute ferric solutions may readily lose their effectiveness for precipitation of phosphate, the capacity of aluminum solutions of comparable strength is unaffected by 2 to 3 hours of aging. This point will be discussed in more detail later in this report.

A set of experiments was conducted at 5°C to explore the effects of temperature on kinetics and extent of phosphate precipitation. These results are presented in Table 2, Experiment Nos. 14 and 15. All other reaction rate studies reported in Table 2 were conducted at ambient temperature (~ 25°C).

Almost all the experiments reported in Table 2 were conducted with a combined solution flow of 65 ml/sec. In some later ambient temperature experiments using both pure orthophosphate solution and actual secondary effluent, the reaction kinetics apparatus was modified so that the time of solution travel to the first sampling port was reduced from 1.3 sec to slightly less than 1 sec. The results of the experiments with pure solutions are presented in Table 2, Experiment Nos. 16 and 17, and those with secondary effluent in Table 2, Experiment Nos. 18 and 19.

In all experiments, the pH of the solution mixture was monitored at port B (see Figure 1) during sample collection. A slight gradual increase in pH was observed in almost all cases. It appears, however, that this rise in pH was due to instrumental factors (probably brought about by the gradual decrease in the rate of solution flow around the pH probe electrode).

In most cases a sample of solution mixture was collected at the discharge point of the kinetics apparatus and flocculated in a Phipps and Bird stirring apparatus.

An examination of the data in Table 2, together with observations made during the course of these tests indicates the following:

1) The residual phosphate in all cases, including tests at 5°C and with secondary effluent, remained essentially constant from the first sampling port through the discharge from the end of the flow line.

Even when samples of the solution mixture discharged from the kinetic apparatus are flocculated by gentle mixing, the growth and agglomeration of the flocs are not accompanied by any additional removal of the phosphate relative to that obtained by millipore filtration through the sample ports.

In fact, as will be discussed in a later section of the report, prolonged periods of flocculation can result in a small increase in the concentration of residual phosphate.

2) Within the sensitivity of the methods employed, in all tests where analysis was made for residual cation [Fe(III) or Al(III)], none could be detected in the filtrates.

3) Under similar conditions, at the same cation-to-phosphate ratio, Al(III) was equally effective when freshly prepared (Table 2, Experiment No. 13) or aged (Table 2, Experiment No. 6).

4) The extent of phosphate removal effected with Fe(III) solutions was strongly dependent on whether freshly prepared (Table 2, Experiment Nos. 10, 11, and 12) or aged (Table 2, Experiment Nos. 1 through 5) solutions were used.

The following conclusions may be drawn from the results of these tests:

1) The reactions between Fe(III) and Al(III) and orthophosphate, which result in the formation of large precipitates and removal of phosphate from solution, are very rapid (complete in less than 1 sec) and may be instantaneous. Apparently nucleation and growth of the precipitate proceeds at least as rapidly as mixing could be effected.

2) The lowering of solution temperature from ambient to 5°C has no measurable effect on the rate of removal of phosphate from solution. Also, the extent of removal of phosphate does not appear to be affected by the change in temperature to any appreciable extent. This is consistent with the conclusion that the rate of the precipitation process was limited by reactant mixing time rather than by time for nucleation and growth of the precipitates.

3) Although no data on the rate of phosphate removal were collected on the reactions of Fe(III) and Al(III) with polyphosphates, the constancy of pH observed in the batch pyrophosphate precipitation experiments (Table 1) indicates that, at or near the pH of optimum phosphate removal, the metal-pyrophosphate reactions are also very rapid.

4) All the Al(III) and Fe(III), at the cation-to-phosphate molar ratios tested, is precipitated with the phosphate or as a hydroxide.

5) Under the conditions tested, dilute Fe(III) solutions, upon aging, rapidly lose their effectiveness for precipitating phosphates from solution. Dilute Al(III) solutions, under test conditions, did not undergo any such loss. Experiments to test this behavior are described in the following section.

6) In the removal of phosphates using aluminum and ferric salts, the need for addition of metal salts in excess of stoichiometric requirements cannot be attributed to the inadequate time which might be permitted for precipitate formation. Instead, as will be discussed later in this report, this can be satisfactorily explained in terms of occurrence of competing reactions and dispersion of the metal-phosphate precipitates into non-settleable and often extremely fine particles.

Hydrolysis of Dilute Al(III) and Fe(III) Solutions and Its Effect on Orthophosphate Precipitation

It was observed in the phosphate removal rate studies that freshly prepared dilute solutions of Fe(III) are considerably more effective than aged solutions in precipitating phosphate, and that this behavior of Fe(III) was

in contrast to that of Al(III). To investigate this phenomenon more thoroughly, various experiments were conducted in which dilute solutions of ferric and aluminum nitrates were prepared and the changes in pH, conductivity and phosphate removal capacity were monitored with time. The procedure followed was described above in the section "Experimental Procedures". The experiments with Fe(III) were continued for periods up to 2.5 days of solution aging, while the behavior of Al(III) was observed over a period of approximately 2 months.

During the aging period the Fe(III) solutions gradually changed color from pale yellow to reddish brown. Rather rapid changes in pH and conductivity were observed. The solution pH dropped from 3.00 to 2.58 during the first 24 hour period. Data on the solution conductivity for the first 6 hours of the test are given in Figure 4(a) where a continuous change is shown. Figure 4(b) shows percent of the initial ferric ion present which passes through a 100 mμ membrane filter. This parameter also shows a steady decrease with time. The results obtained when aged Fe(III) solutions were used to precipitate orthophosphate are shown in Figure 4(c). A steady drop of removal capacity with time may be noted. In the phosphate precipitation experiments, readily settleable flocs were formed in all cases. However, in contrast to the pale yellow color of the precipitates obtained in the experiments with fresh iron solutions, the precipitates formed in the experiments with aged iron were more reddish.

In contrast to the behavior of Fe(III) an unacidified dilute solution of Al(III) was found to be stable over a 2-month observation period. No changes in pH, conductivity and the capacity to precipitate phosphate were

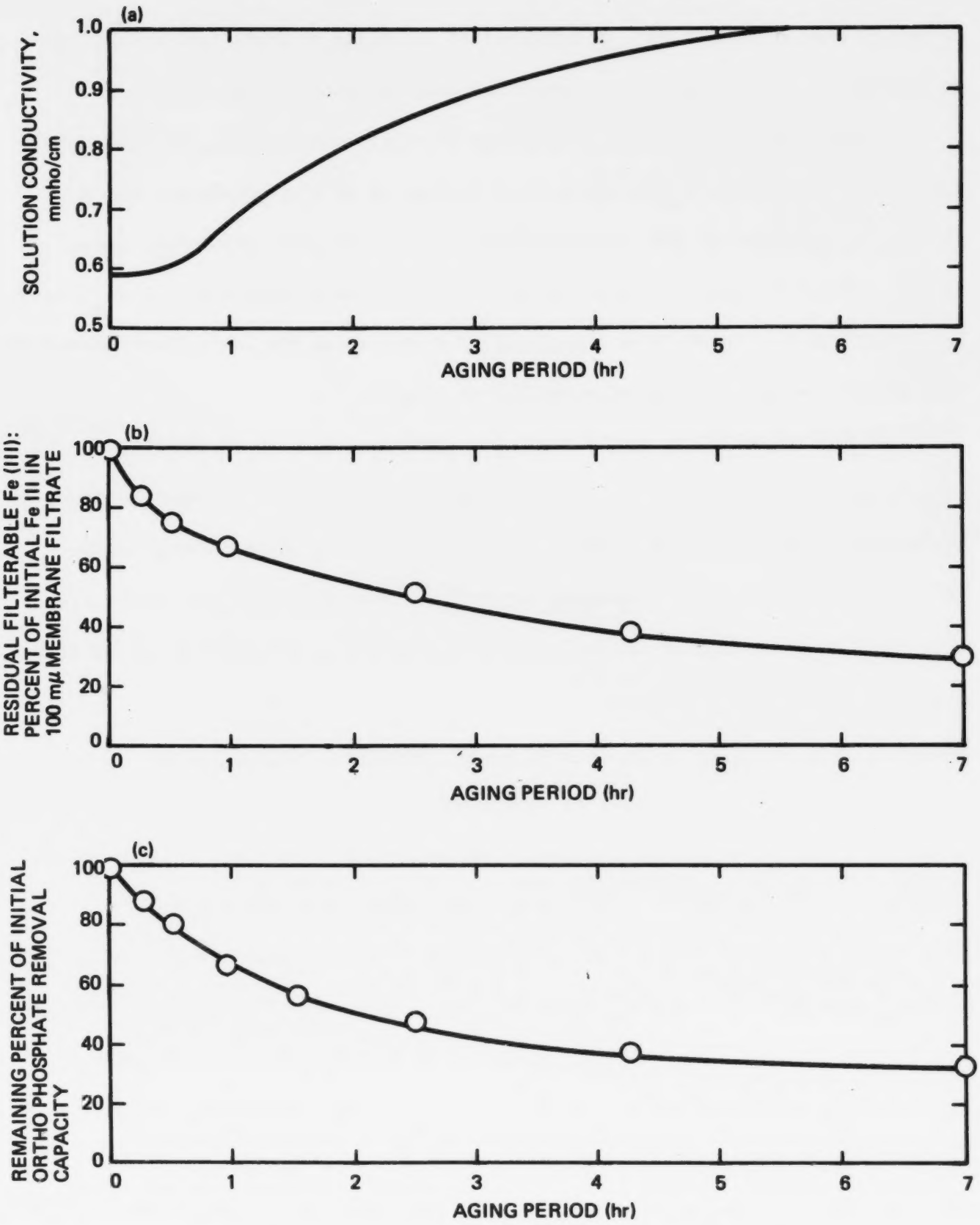

Figure 4. Effect of Aging on Properties of a Dilute (7.72×10^{-4} M) Fe (III) Solution

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observed when a 7.72×10^{-4} M solution of aluminum nitrate (pH = 4.0, conductivity = 0.31 mmhos/cm) was aged for this period of time.

These results indicate that under the test conditions, Fe(III) undergoes rapid hydrolysis, resulting in a darkening of the solution, and a change in solution pH and conductivity. The hydrolysis products, i.e., ferric hydroxide, grow in size so as to be removable with the 100 mμ filter. The hydrolysis process is accompanied by a reduction in the effectiveness of the Fe(III) solution in precipitating phosphates.

On the other hand, under similar conditions but at an initial pH one unit higher (4.0 compared to 3.0), the Al(III) exhibited no such tendency to hydrolyze. (At higher pH levels, e.g., 6.0, Al(III) does undergo such hydrolysis). This lower tendency of Al(III) toward hydrolysis correlates with the observed higher optimal pH for phosphate precipitation by Al(III) salts.

Effect of Flocculation Time on Removal of Phosphate with Fe(III)

The effect of flocculation time ("aging" of the precipitate) on the extent of removal of phosphate following addition of an Fe(III) salt solution to an orthophosphate solution was evaluated in a batch "jar test" experiment (method described in the Section "Experimental Procedures"). An initial phosphate concentration of 12 mg/ℓ P and a 1:1 Fe(III)/PO_4^{-3} molar ratio were used at a pH of 5.0. Aliquots of the mixture were removed at various time intervals while the mixture was being flocculated (slow mixing). These aliquots were immediately vacuum filtered through 450 mμ membrane filters. The filtrates were analyzed for residual phosphate concentrations. The pH of the solution mixture which was monitored during this 6½-hour experiment showed no measurable change. To minimize the dissolution of atmospheric CO_2, a stream of nitrogen was kept directed on the surface of the

solution in the reaction beaker during the course of the experiment. The temperature was maintained at 25.0°C using a water bath. The concentration of residual phosphate in the filtrates showed a gradual increase with flocculation time from the initial 3.12 mg/ℓ P to 3.56 mg/ℓ P after 6.25 hours. This may be caused by an hydrolysis reaction, producing a more basic ferric compound and soluble phosphate. Also, a possibility exists that it was caused by dispersion of the phosphate precipitate so that some is not removed by membrane filtration.

Parametric Study of Orthophosphate Precipitation

Using the "jar test" method (described above in the section "Experimental Procedures"), a study was made of the effect of pH and reactant molar ratio on the precipitation of orthophosphate by Al(III) and Fe(III) salts. The results of the initial studies are presented in Figures 5, 6, and 7. In these experiments, pH adjustment was made by raising the phosphate test solution pH prior to addition of Al(III) or Fe(III) salt solution. Figure 5 shows residual phosphate as a function of pH for both Fe(III) and Al(III) for a 0.5:1 cation-to-phosphate molar ratio. Figure 6 shows this for a 1:1 molar ratio, while Figure 7 shows it for a 2:1 molar ratio. More recent results where the pH adjustment was made concurrent with addition of the precipitating solution are shown in Figures 8 through 13. Figures 8, 9, and 10 show, respectively, the residual turbidity, residual orthophosphate, and residual Fe(III) with the latter used at a 1:1 molar ratio, all as functions of pH. Figures 11, 12, and 13, respectively, show corresponding data for Al(III).

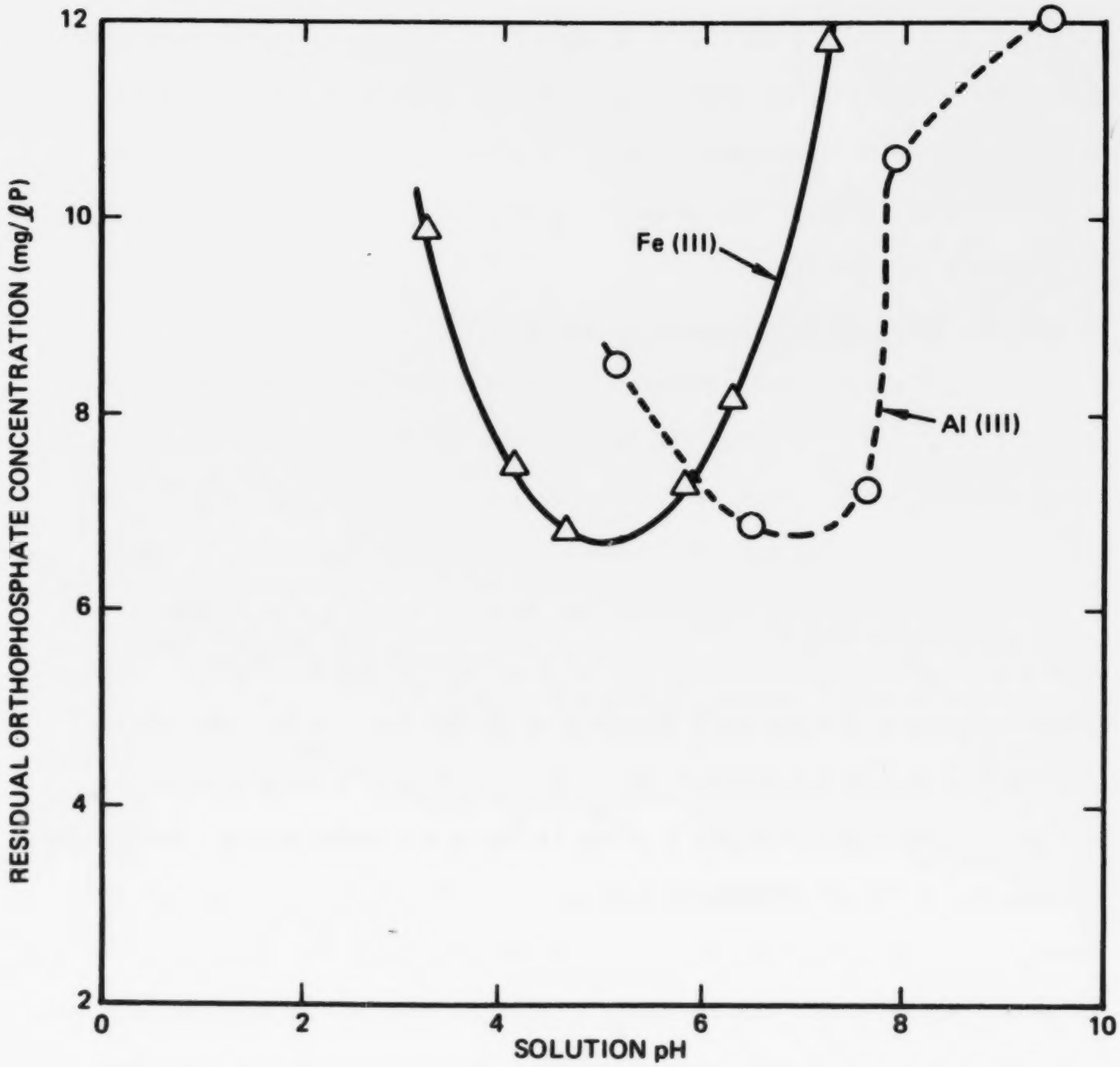

Figure 5. Precipitation of Orthophosphate with Al (III) and Fe (III) at a 0.5:1 Cation-to-Orthophosphate Molar Ratio (Initial Orthophosphate Concentration, 12 mg/ℓP)

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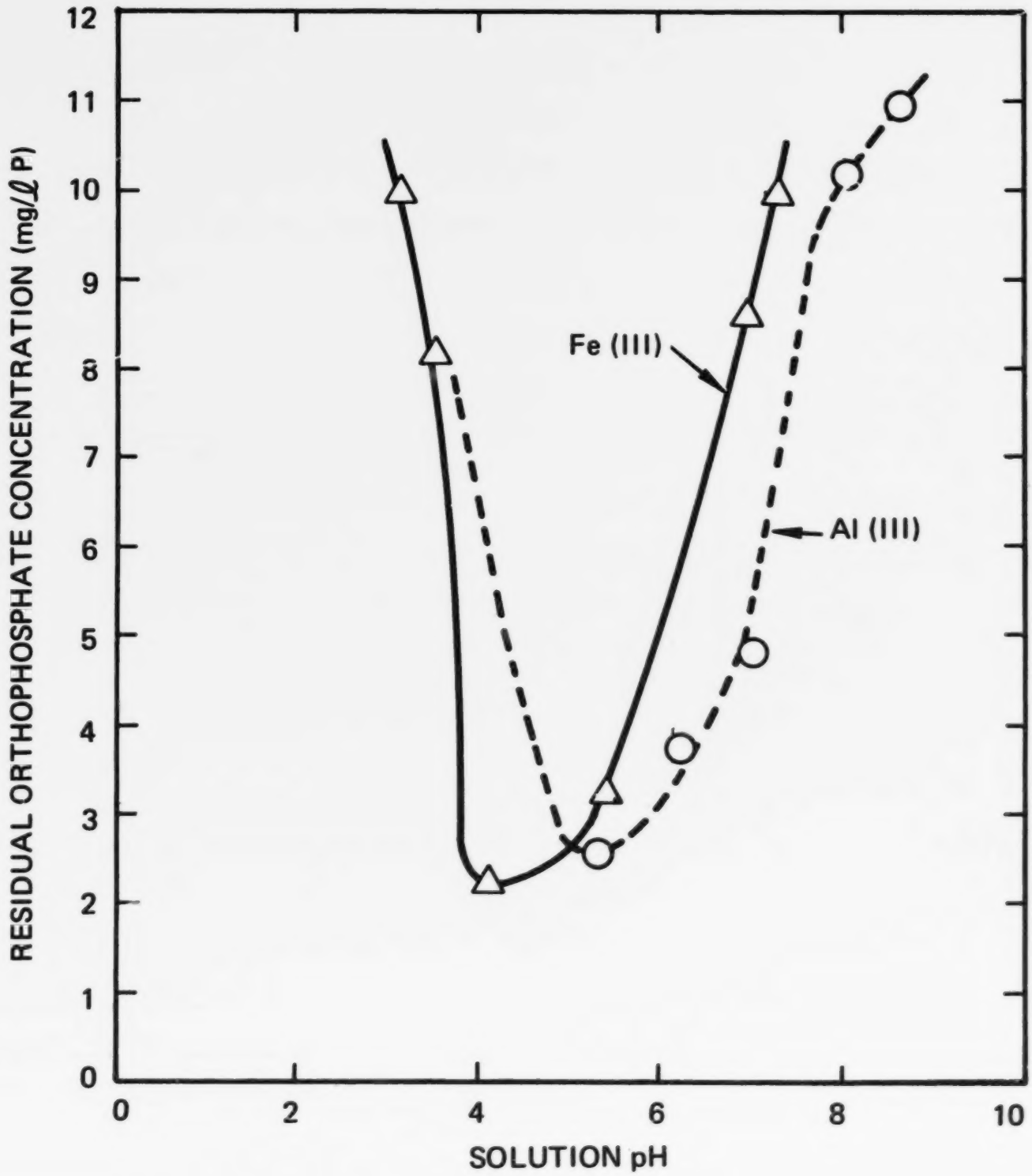

Figure 6. Precipitation of Orthophosphate with Al (III) and Fe (III) at a 1: 1 Cation-to-Orthophosphate Molar Ratio
(Initial Orthophosphate Concentration, 12 mg/ℓ P)

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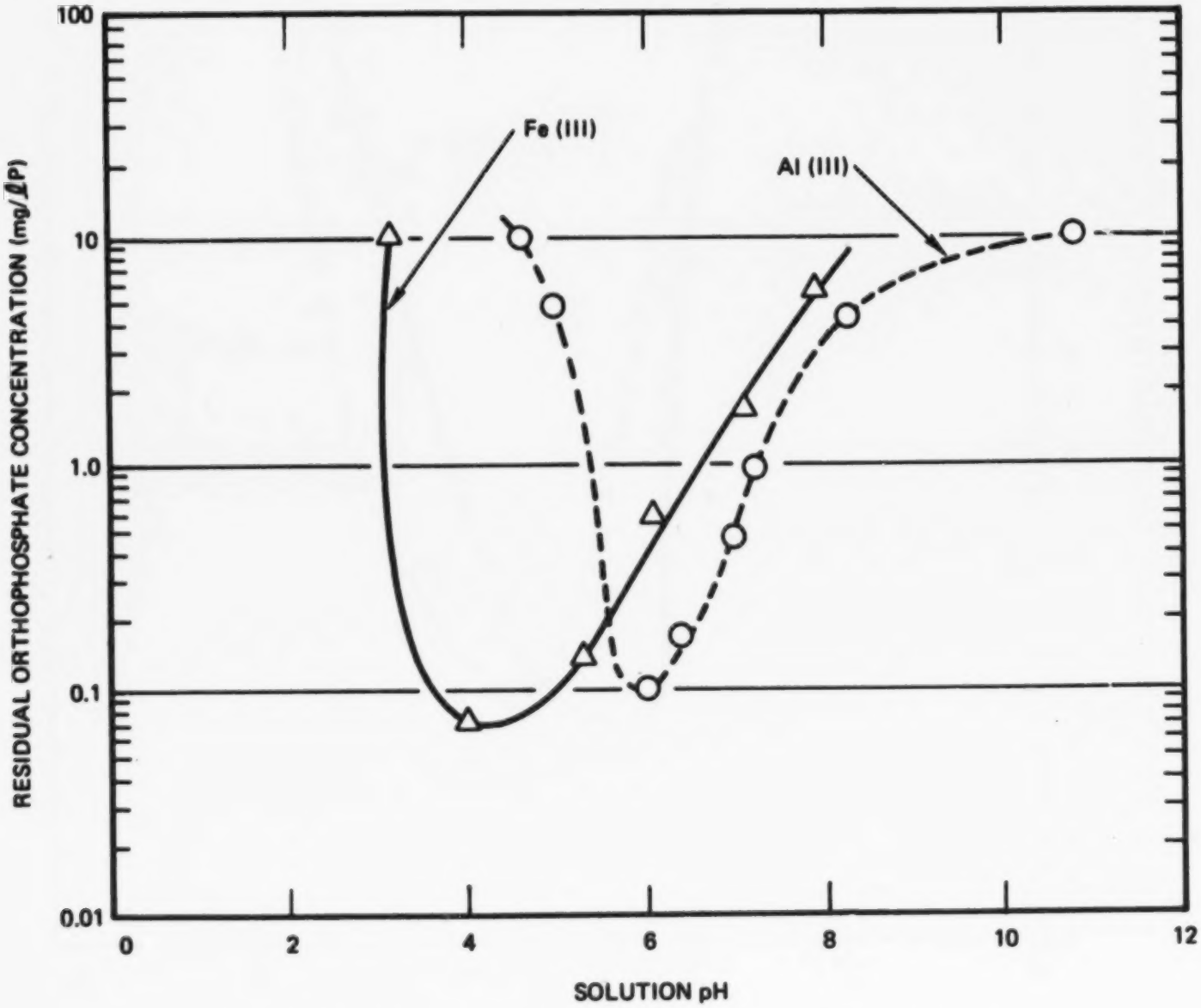

Figure 7. Precipitation of Orthophosphate with Al (III) and Fe (III) at a 2:1 Cation - to - Orthophosphate Molar Ratio (Initial Orthophosphate Concentration, 12 mg/ℓP)

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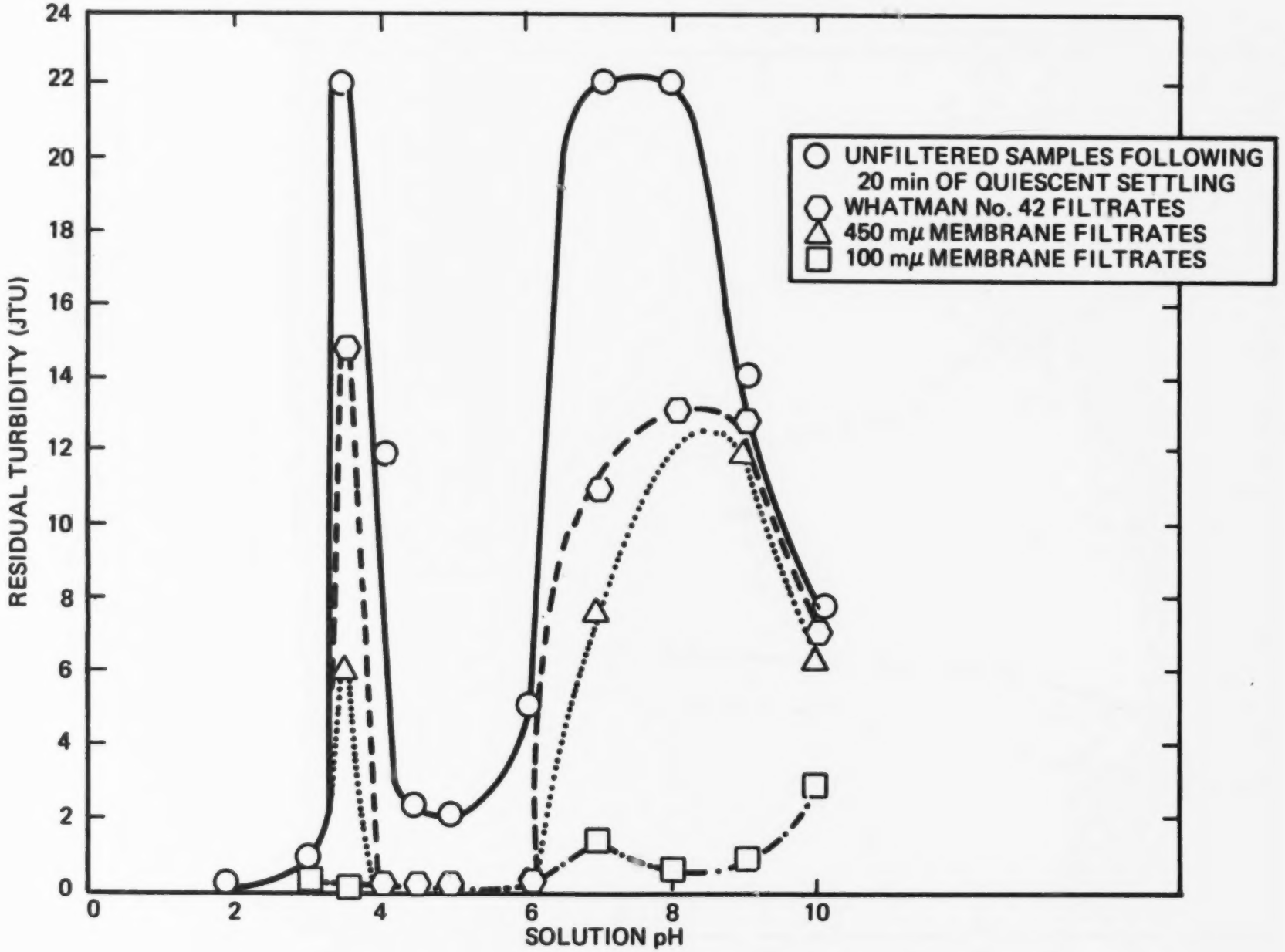

Figure 8. Residual Turbidity in Precipitation of Orthophosphate with Fe (III) at a 1:1 Cation-to-Orthophosphate Molar Ratio (Initial Orthophosphate Concentration, 12 mg/ℓP)

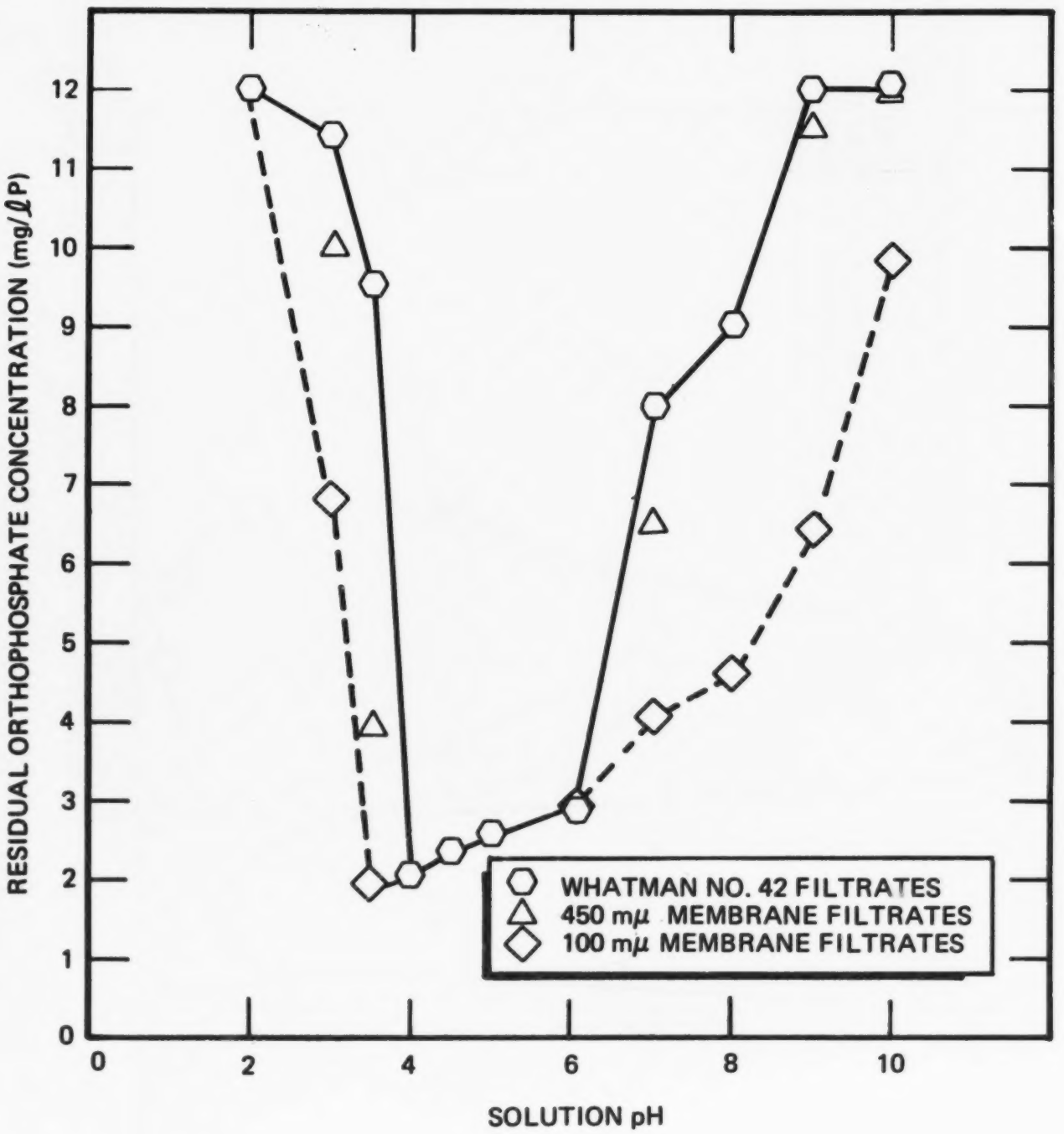

Figure 9. Residual Orthophosphate in Precipitation of Orthophosphate with Fe (III) at a 1:1 Cation-to-Orthophosphate molar ratio (Initial Orthophosphate Concentration, 12 mg/ℓ P)

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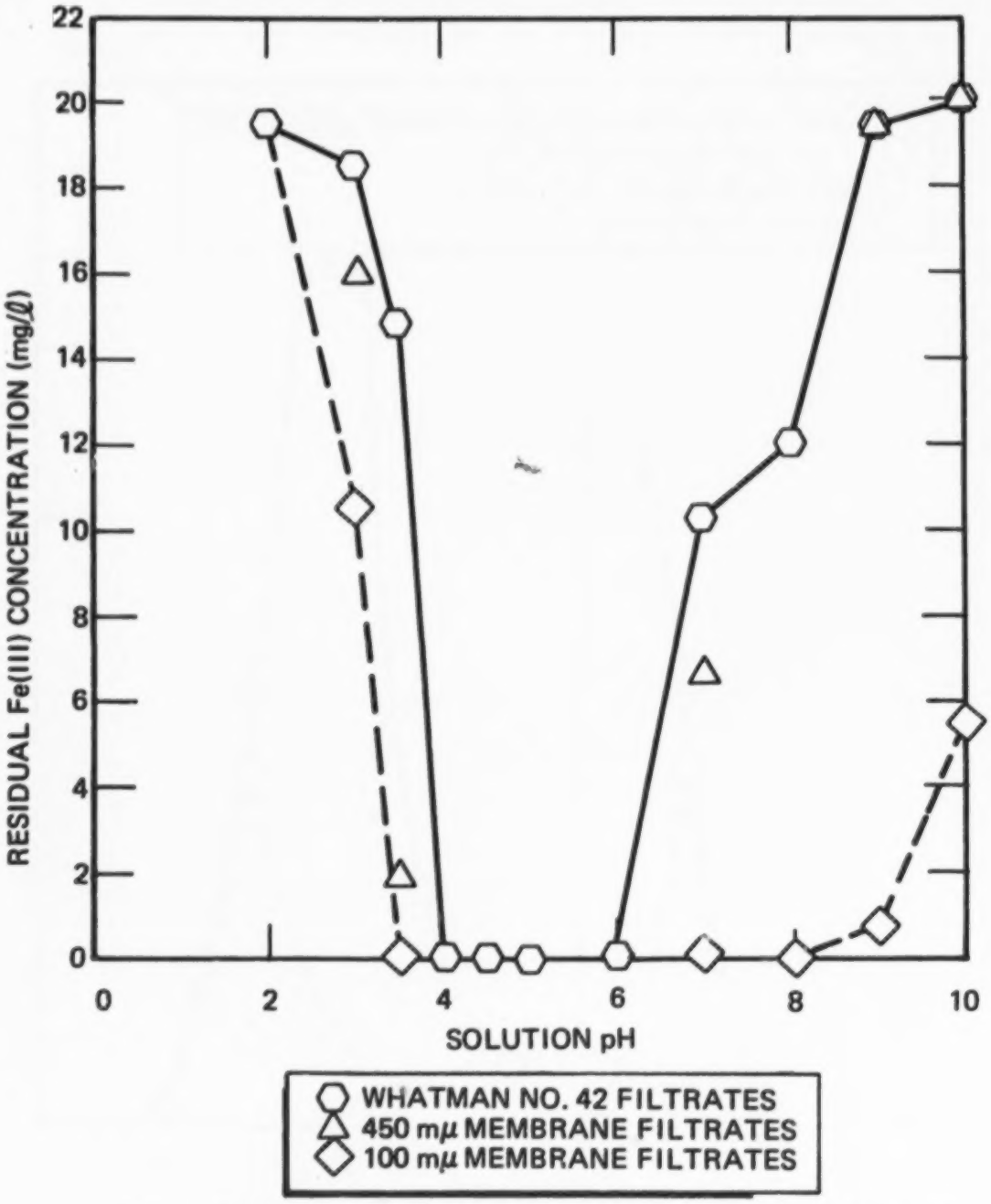

Figure 10. Residual Fe(III) in Precipitation of Orthophosphate with Fe(III) at a 1:1 Cation-to-Orthophosphate Molar Ratio (Initial Orthophosphate Concentration, 12 mg/ℓP)

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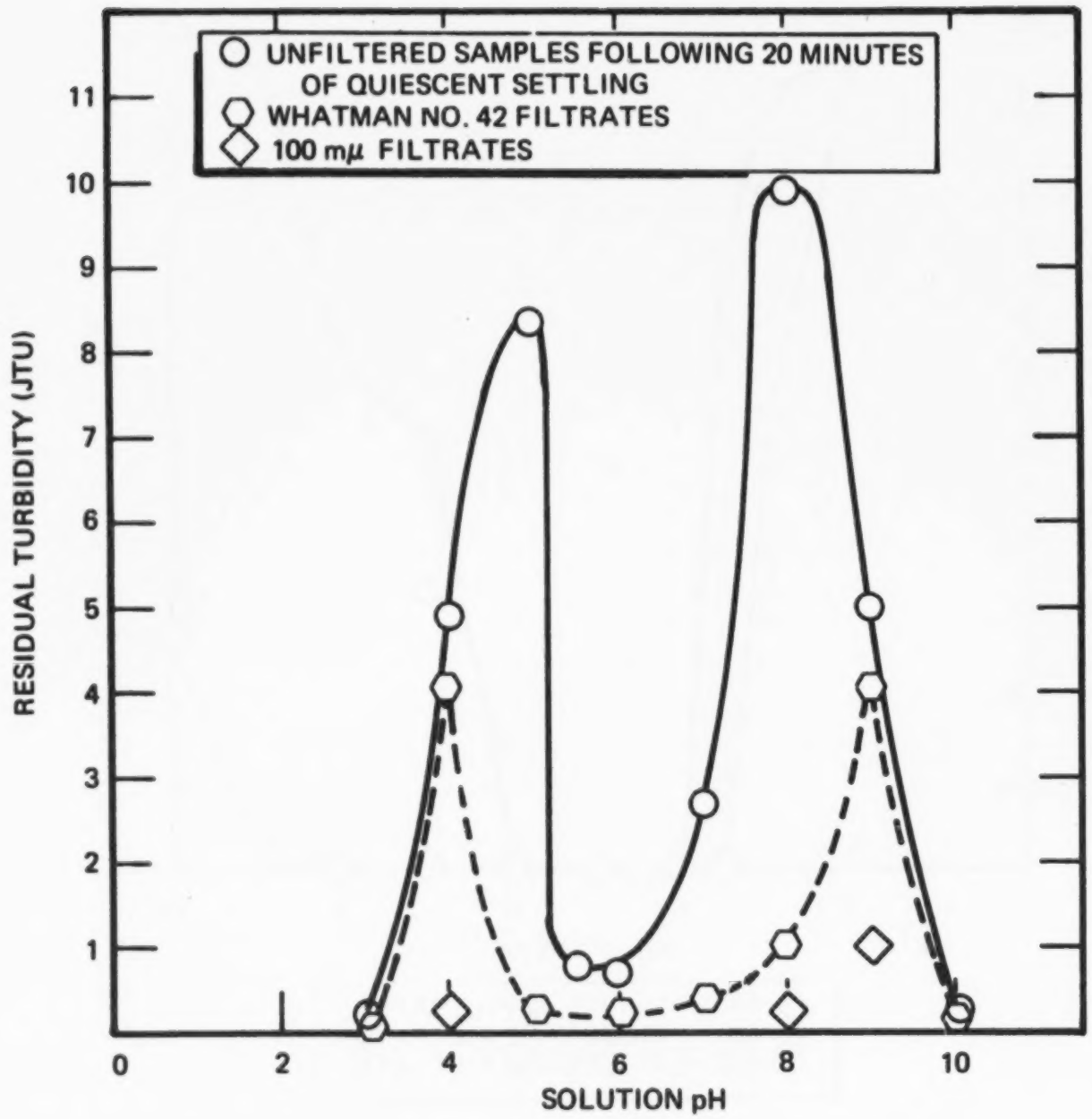

Figure 11. Residual Turbidity in Precipitation of Orthophosphate with A1(III) at 1:1 Cation-to-Orthophosphate Molar Ratio (Initial Orthophosphate Concentration, 12 mg/ℓP)

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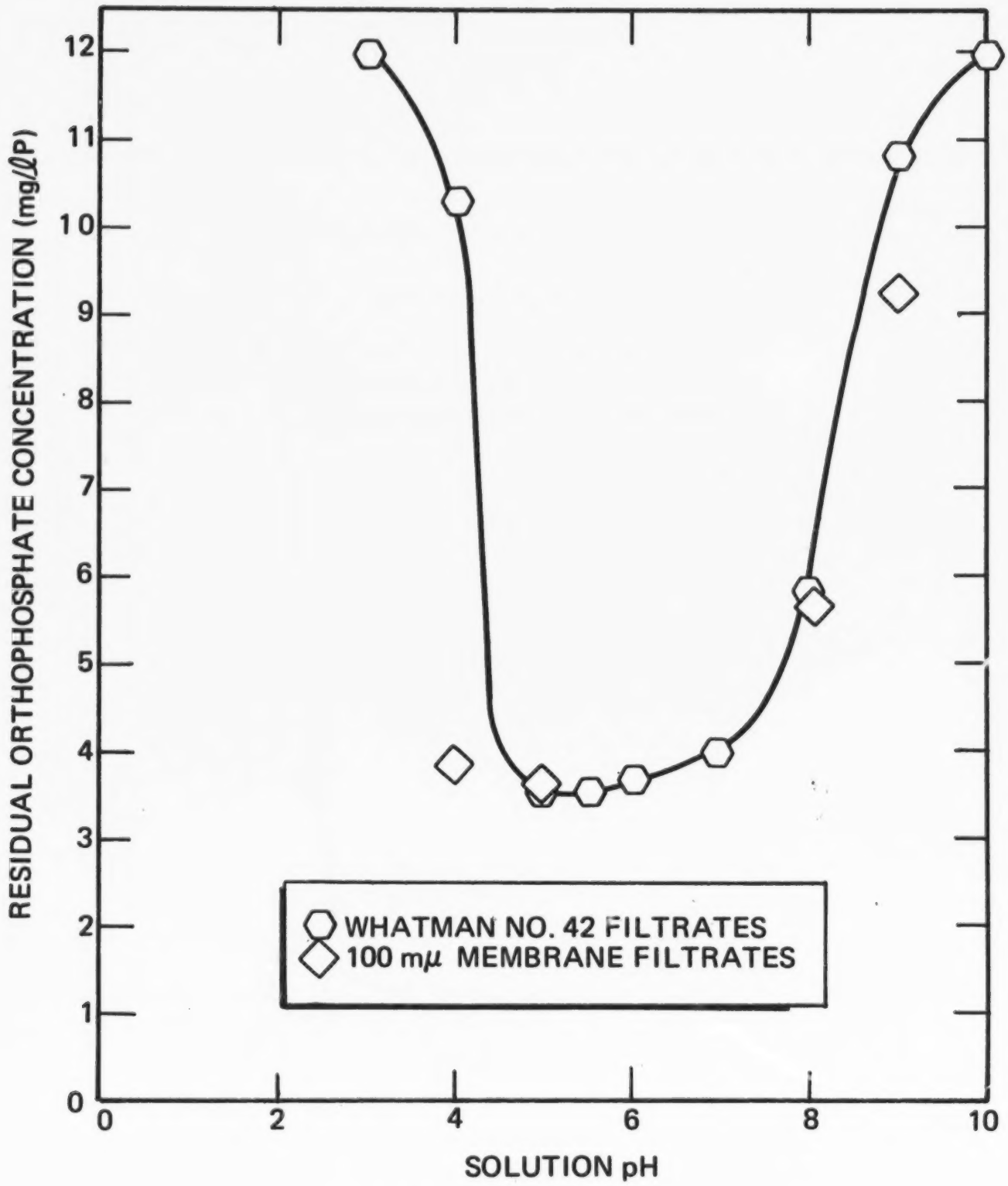

Figure 12. Residual Orthophosphate in Precipitation of Ortnophosphate with Al (III) at a 1:1 Cation-to-Orthophosphate Molar Ratio (Initial Orthophosphate Concentration, 12 mg/ℓ P)

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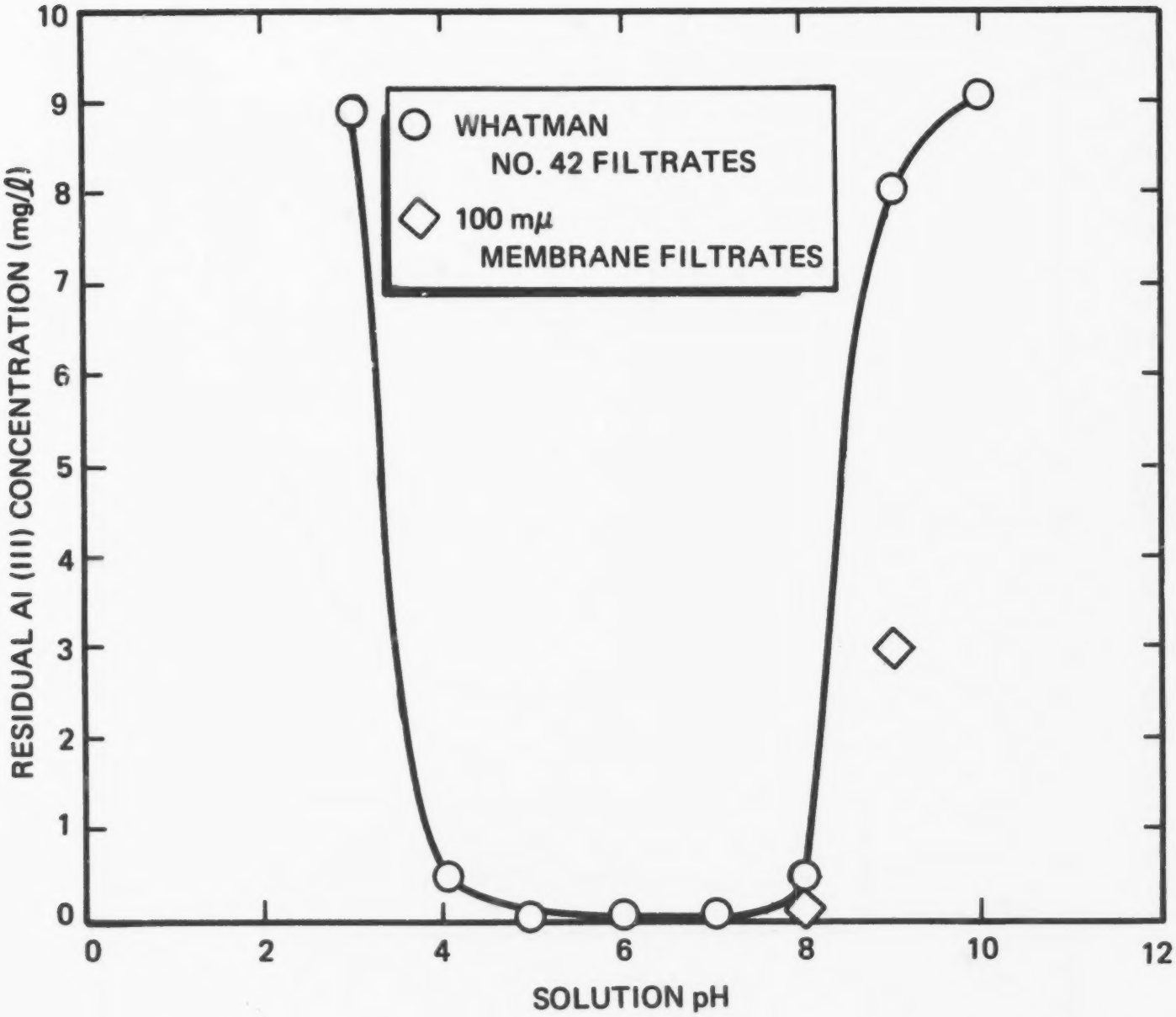

Figure 13. Residual Al (III) in Precipitation of Orthophosphate with Al (III) at a 1:1 Cation-to-Orthophosphate Molar Ratio (Initial Orthophosphate Concentration, 12 mg/ℓ P)

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Comparison of the results shown in Figures 6 and 9 indicate that in the case of Fe(III) the extent of phosphate removal is unaffected by the manner of pH adjustment (i.e., prior to or concurrent with the addition of Fe(III)). In the case of aluminum (compare Figures 6 and 12), the results are generally the same for both methods of pH adjustment. However, in the pH region from ~ 6 to 9, higher phosphate removals are apparently obtained when the adjustment of pH is concurrent with the addition of the precipitant.

From the results presented, the efficiency of phosphate removal may be seen to be a very strong function of solution pH. The optimum pH for phosphate precipitation is about 4.0 (actually near 3.5, if filtration through a 100 mμ membrane is used for separation, see Figure 9) for ferric salts, and is near 5.0 for aluminum salts (Figure 12) at the concentrations used. At the pH of maximum phosphate precipitation, the removal of phosphate affected by Fe(III) is greater than that by Al(III).

Data on the turbidity of product solutions from the cation-orthophosphate reactions, presented in Figure 8 and 11, show the following. At the pH for optimum phosphate precipitation and at slightly lower pH levels, the cation-orthophosphate reactions result in the formation of turbidity which does not setile very well. In the case of Fe(III) at a pH in the range from 3 to 4, it could only be removed effectively by filtration through a very fine (100 mμ) membrane. Within the pH range of approximately 5 to 7 for Al(III) and 4 to 6 for Fe(III), large gelatinous precipitates are formed which settle out very readily. Further increases in pH, however, result in an increase in settled solution turbidity. In the case of Fe(III), the degree of interaction between Fe(III) and orthophosphate gradually decreases

as the pH is raised above 6.0; eventually only colloidal turbidity which is formed by Fe(III) hydrolysis is produced. The degree of fineness (dispersion) of the colloidal precipitates in the Fe(III) system also increases as the pH is raised, since as indicated in Figure 8 at pH 10, turbidity could not be completely eliminated even by filtration through 100 mμ filters. The behavior of the Al(III)-orthophosphate system under alkaline conditions is similar to that observed for the corresponding Fe(III)-orthophosphate system. Although in both cases the degree of cation-orthophosphate interaction decreases as the pH is raised, the turbidity developed in the pH 7-9 region with Fe(III) appears to be more finely divided as evidenced by its passing through Whatman No. 42 paper. At very low pH levels (less than 3 for aluminum, and less than 2 for iron) where no turbidity was observed, either there are no reactions between these cations and orthophosphate, or the reactions result in the formation of soluble metal-phosphate complexes.

The data on the residual Fe(III) and Al(III) concentrations presented in Figures 10 and 13 show that the removal of the phosphate is accompanied by complete precipitation of the Fe(III) at pH levels greater than 3.5. (No Fe(III) could be detected in the filtrates even when, in some cases, the filtrates were concentrated by a factor of 10.) A residual Al(III) concentration of less than 0.1 mg/ℓ Al was observed within the pH range of 5 to 7, that of optimum phosphate removal with Al(III).

Stoichiometry of Cation-Orthophosphate Reactions at Constant pH

To supplement the results on phosphate removal presented above, the removal of orthophosphate by reaction with Fe(III) and Al(III) was studied at constant pH values of 4.0 and 5.0 [Fe(III)] and 6.0 [Al(III)] over a

wide range of cation-to-orthophosphate molar ratios. The results of the study of the Fe(III)-orthophosphate reaction are presented in Figures 14 through 18, in which reactant removal (or residual) and settled turbidity for the series of measurements are plotted against reactant molar ratios. Phosphate removal and settled turbidity are given in Figure 14 for the study at pH = 5.0. Figure 15 shows the phosphate removal obtained, and its dependence on the fineness of the filter medium as functions of molar ratio (pH = 4.0) when the product solutions are filtered through 450 mμ and 100 mμ membrane filters as well as Whatman No. 42 filter paper. Figure 16 shows residual solution turbidity for the pH = 4.0 study as a function of molar ratio, and its variation with the fineness of the filter medium used. Figure 17 shows residual iron (Fe(III)) as a function of the same parameters. Figure 18 shows the phosphate removal obtained in a study at pH = 5.0 when the amount of Fe(III) added, and therfore its initial concentration in the reactant solution, was kept constant while the initial phosphate concentration was raised.

The data in Figures 14 and 15 show that at constant pH, the removal of phosphate at pH 4.0 and pH 5.0 is directly proportional to the amount of added iron up to an Fe(III)/PO_4^{-3} ratio of about 1.2:1. Complete precipitation of phosphate is achieved at Fe(III)/PO_4^{-3} ratios of 1.4-1.6 and higher. The existence of such a linear relationship between the amount of added Fe(III) and the phosphate removal obtained over such a wide range of added Fe(III), strongly suggests that the reaction between Fe(III) and orthophosphate, which results in the formation of precipitate and removal of the phosphate, proceeds as a purely homogeneous chemical reaction and not by a

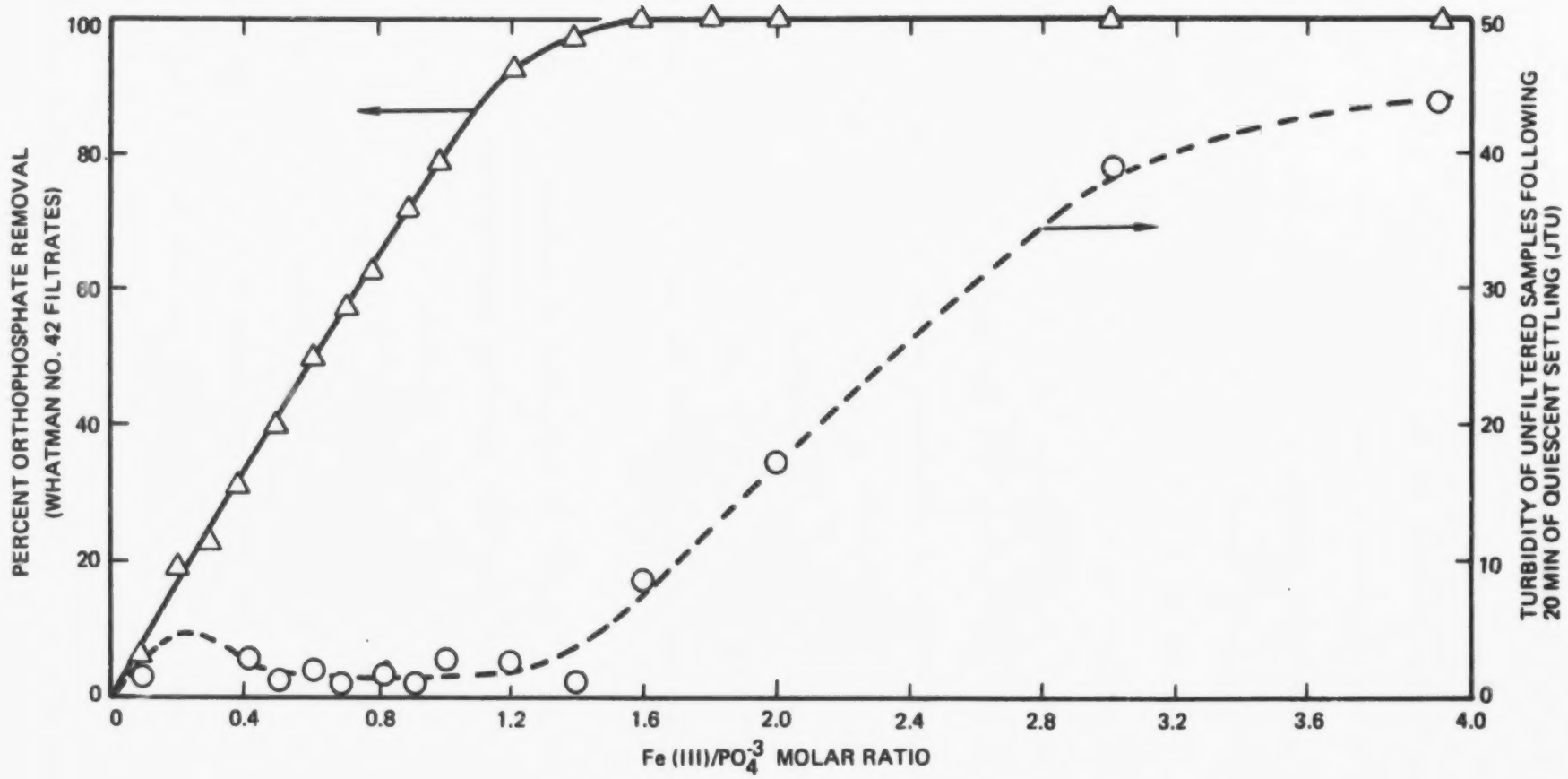

Figure 14. Fe (III)-Orthophosphate Reaction at pH 5.0
(Initial Orthophosphate Concentration, 12 mg/ℓP)

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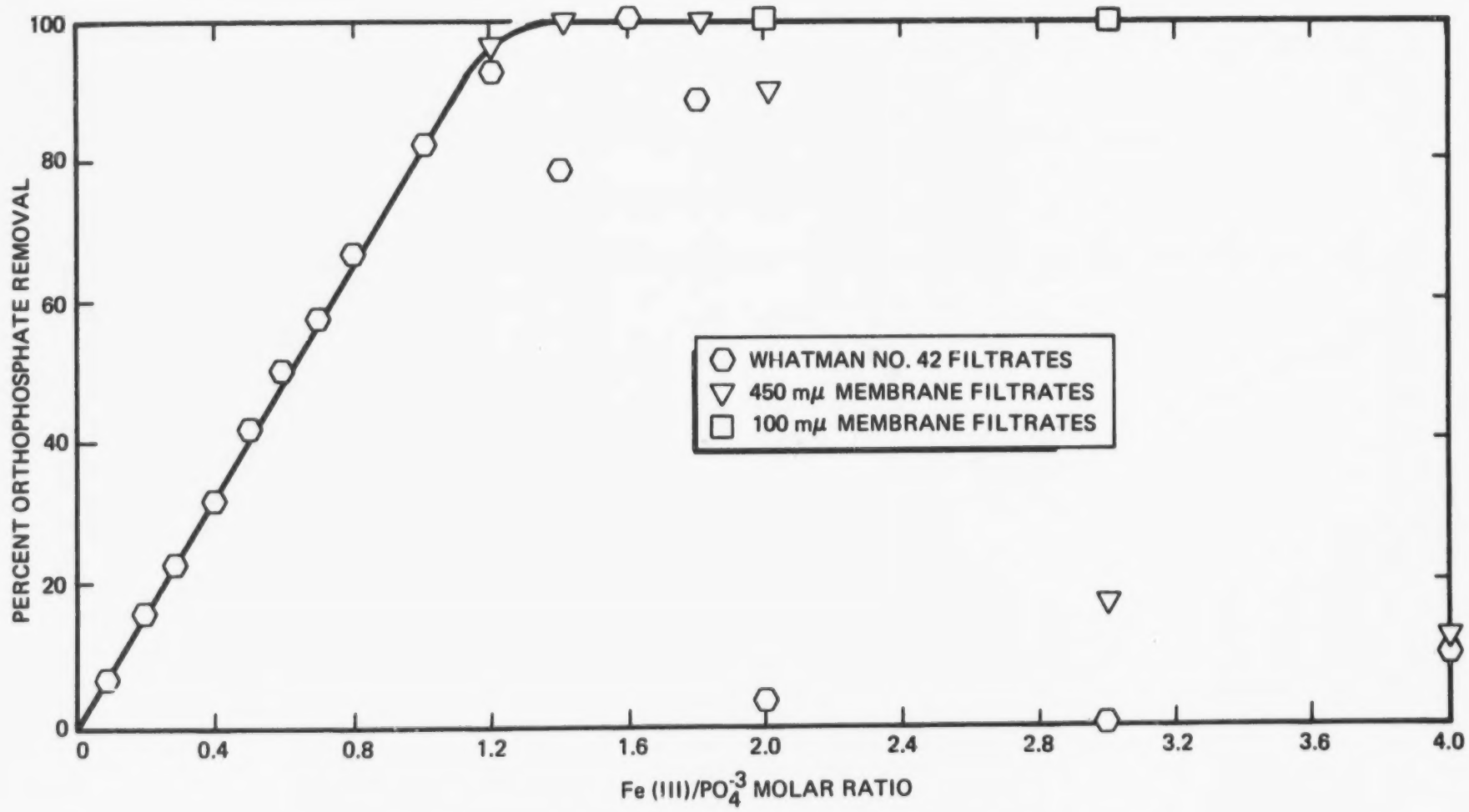

Figure 15. Orthophosphate Removal in Fe (III)-Orthophosphate Reaction at pH 4.0
(Initial Orthophosphate Concentration, 12 mg/ℓP)

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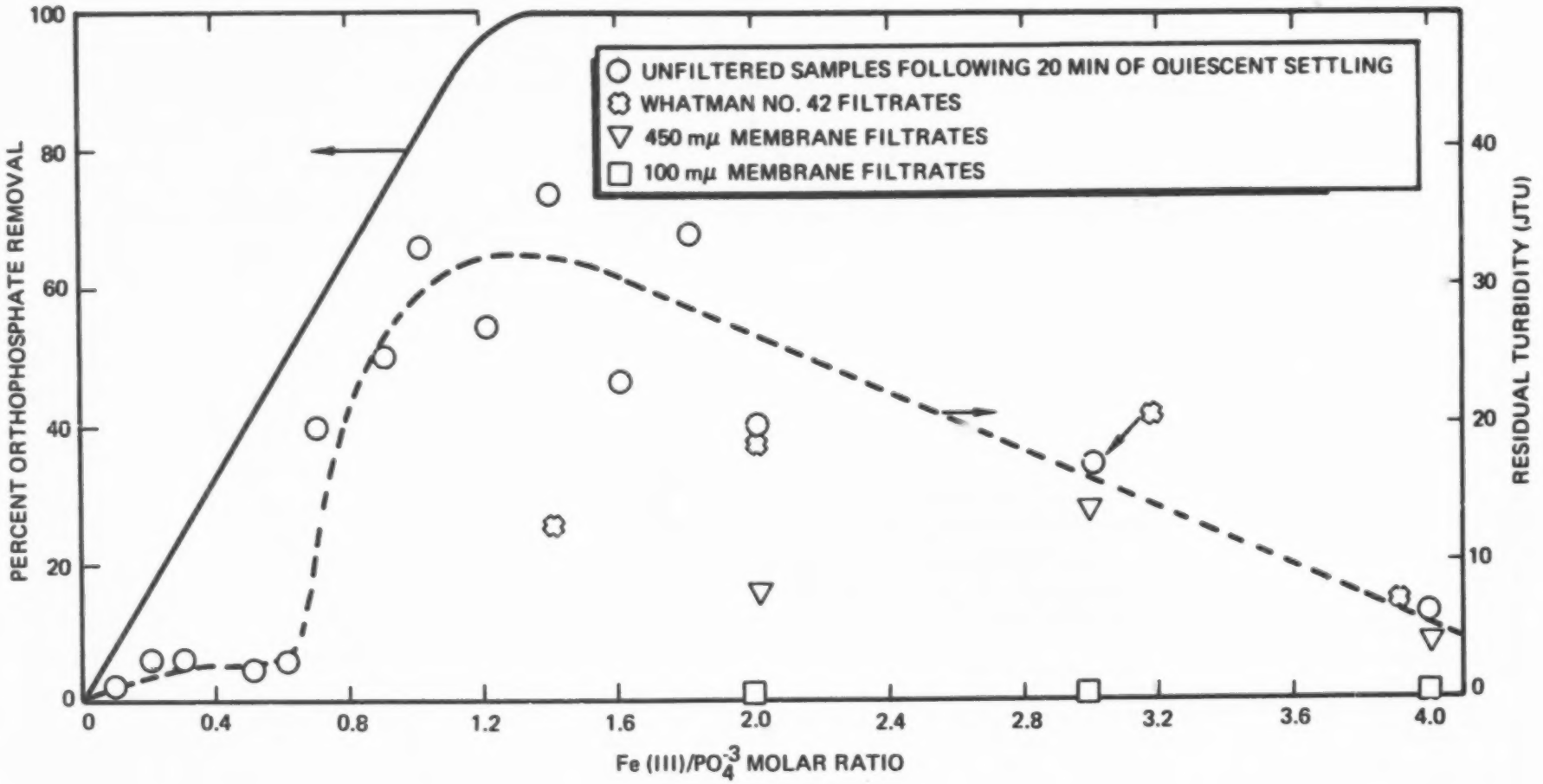

Figure 16. Orthophosphate Removal and Residual Turbidity in Fe (III)-Orthophosphate Reaction at pH 4 (Initial Orthophosphate Concentration, 12 mg/ℓP)

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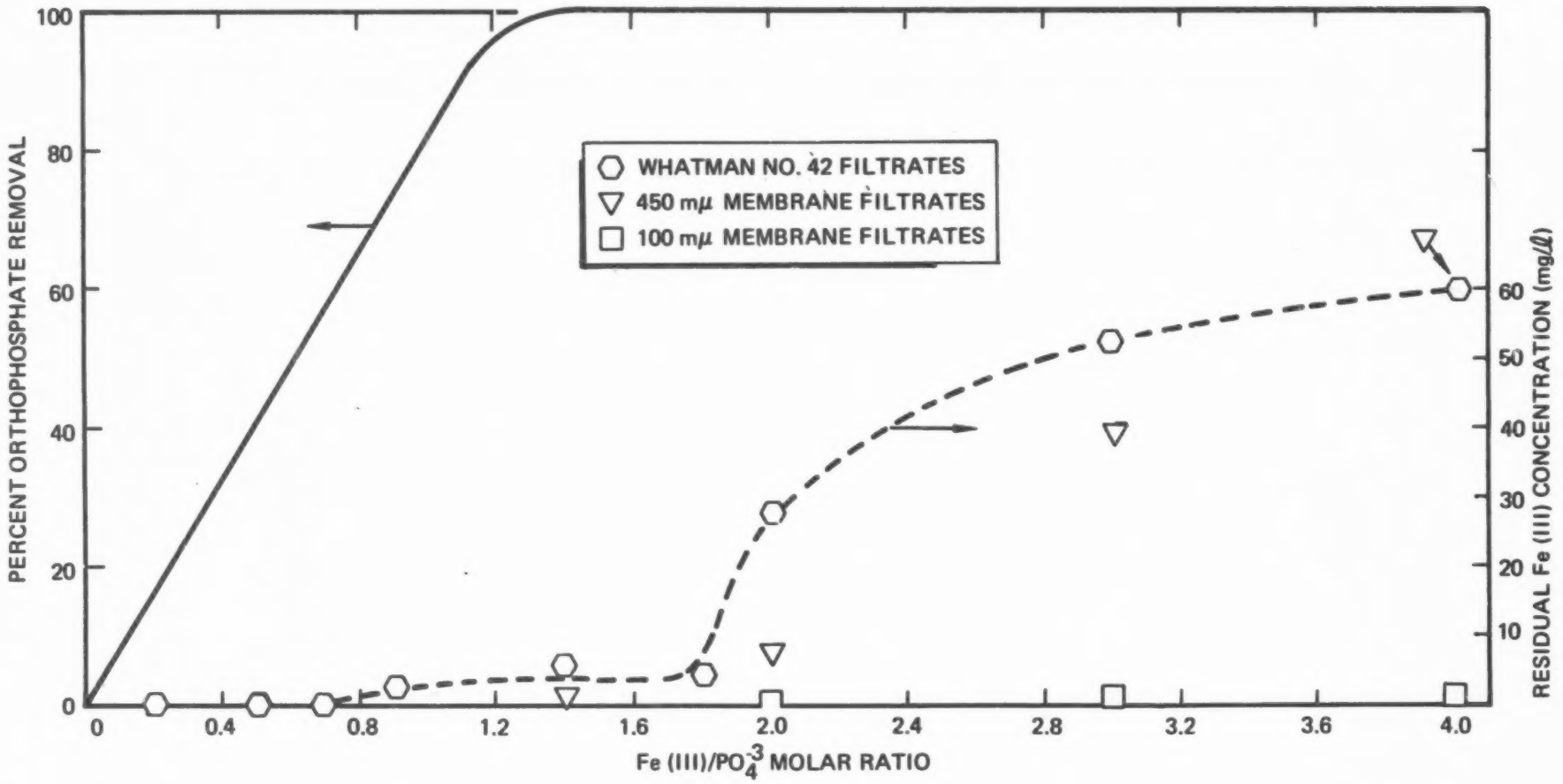

Figure 17. Residual Fe (III) in Fe (III)-Orthophosphate Reaction at pH 4.0
(Initial Orthophosphate Concentration, 12 mg/ℓP)

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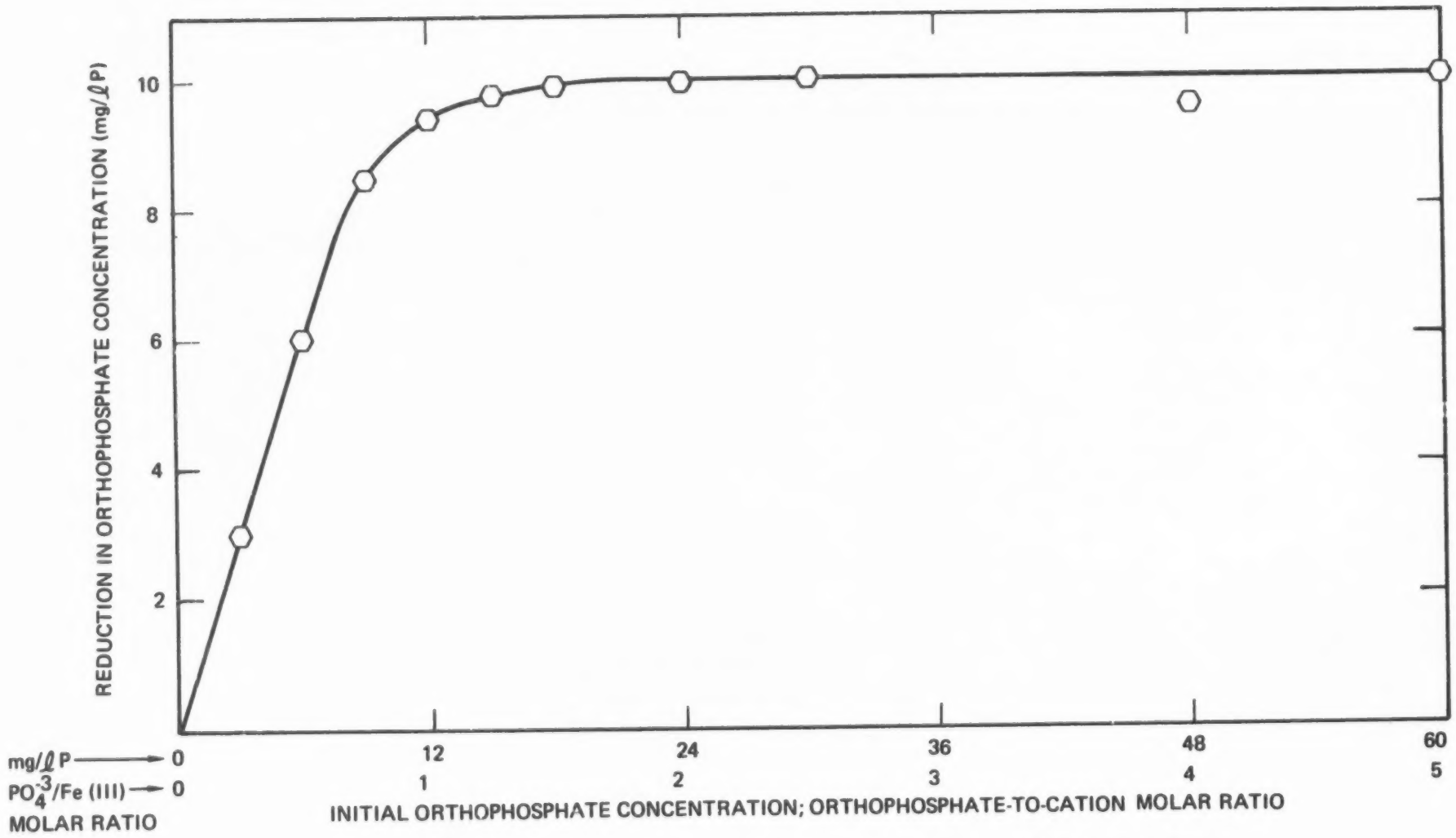

Figure 18. Orthophosphate Removal by Fe (III) at pH 5.0 as a Function of Initial Orthophosphate Concentration [Initial Fe (III) Concentration, 21.6 mg/ℓ (3.86×10^{-4} M)]

70-A1-032-25

heterogeneous mechanism involving adsorption (physical or chemical) of phosphate on precipitating ferric hydroxide.

Since the ratio of added Fe(III) to PO_4^{-3} removed is greater than 1:1, it appears that one or more hydrolysis products of Fe(III) (e.g., $Fe(OH)_2^{+}$, $Fe(OH)^{+2}$, etc.) and not the Fe^{+3} species alone are involved in the precipitate formation. Such a hypothesis is consistent with the finding that aged (hydrolyzed) solutions of Fe(III) are less effective in precipitating phosphates than fresh (less hydrolyzed) iron solutions. In this study, it was observed that the reaction of Fe(III) with phosphate at pH 5.0 results in the formation of large settleable flocs at all Fe(III)/PO_4^{-3} ratios less than 1.5. Further increases in the amount of added iron salt resulted in an impairment of the precipitate settleability and thus an increase in the amount of residual turbidity as indicated in Figure 14. In all cases examined, however, the particles formed were large enough to be removed by filtration through Whatman #42 filter paper. The turbidity in samples with Fe(III)/PO_4^{-3} ratios of 3.0 and 4.0 was observed to agglomerate into large gelatinous reddish precipitates after 1-2 hours of stand time.

As indicated in Figure 16, the onset of the development of poorly settleable flocs at pH 4.0 occurs at a lower Fe(III)/PO_4^{-3} ratio (0.8:1) than at a pH of 5.0, and further increases in the concentration of added Fe(III) result in the dispersion of the precipitates into an extremely fine colloid. The degree of dispersion and colloidal fineness was observed to increase with the increase in the Fe(III)/PO_4^{-3} ratio. Thus, while at a Fe(III)/PO_4^{-3} ratio of 2.0 most of the colloidal particles not removed by Whatman #42 filtration could be retained by a 450 mμ membrane filter, at a Fe(III)/PO_4^{-3} ratio of 4.0 the colloid could only be removed by filtration through a much finer (100 mμ) membrane filter.

Analysis of the Whatman #42 filtrates obtained in the experiments at pH 5.0 for the residual Fe(III) content showed that, except at a Fe(III)/PO_4^{-3} ratio of 4:1 where a residual iron concentration of 1.1 mg/ℓ was detected, the Fe(III) content of all filtrates were less than 0.05 mg/ℓ. Since essentially all values were about 0, the results are not shown in Figure 14. The data for residual Fe(III) for the pH 4.0 experiments are plotted in Figure 17. At Fe(III)/PO_4^{-3} molar ratios of 2.0 and greater, only those filtrates obtained by filtration through 100 mμ membrane filters were devoid of iron. The increased dispersion of the Fe(III)/PO_4^{-3} precipitate at high Fe(III)/PO_4^{-3} molar ratios also led to a corresponding increase in the concentration of residual Fe(III) (and phosphate) in the filtrates obtained by filtration through Whatman #42 paper and 450 mμ membrane filters.

The effect of phosphate concentration on the extent of phosphate removal at pH 5.0 was also studied using a constant initial Fe(III) concentration of 3.86×10^{-4} M and PO_4^{-3}/Fe(III) molar ratios ranging from 0.25:1 to 5.0:1. The results are shown in Figure 18, which gives residual phosphate vs PO_4^{-3}/Fe(III) ratio, and Table 3 which gives residual turbidity, phosphate and Fe(III) at lower molar ratios and their dependence on the fineness of the filter medium used. Quantitative precipitation of phosphate was observed at PO_4^{-3}/Fe(III) ratios of 0.25:1 and 0.5:1. At these reactant ratios, the presence of excess Fe(III) resulted in the formation of turbidity which could only be effectively removed by filtration through a 100 mμ membrane (see Table 3). The results shown in Table 3 indicate that this fine turbidity is primarily that of iron compounds which do not contain any phosphate. At PO_4^{-3}/Fe(III) ratios of 0.75:1 and greater, large

TABLE 3

RESULTS OF ORTHOPHOSPHATE-Fe(III) REACTION AT pH 5.0 FOR LOW PO_4^{-3}/Fe(III) MOLAR RATIOS

PO_4^{-3}/Fe(III) Molar Ratio	Residual Turbidity (JTU)				Residual P (mg/ℓ)		Residual Fe(III) (mg/ℓ Fe)		
	(1)	(2)	(3)	(4)	(2)	(3)	(2)	(3)	(4)
0.25:1	4	4	3.5	0.25	< 0.01	< 0.01	15.5	10.5	~ 0
0.50:1	4.6	4.3	3.7	1.7	< 0.01	< 0.01	15.7	10.0	~ 0

(1) Unfiltered sample following 20 min of quiescent settling

(2) Whatman #42 filtrates

(3) 450 mμ membrane filtrates

(4) 100 mμ membrane filtrates

settleable precipitates were formed. Accordingly, the Whatman #42 filtrates from these experiments were all free from turbidity and contained no Fe(III). The data shown in Figure 18 indicate that at all PO_4^{-3}/Fe(III) ratios greater than 1.5:1 only a fixed amount of phosphate is removed irrespective of the initial (or equilibrium) phosphate concentration. This constitutes additional support for the conclusion that the Fe(III)-orthophosphate reaction involves compound formation and does not involve adsorption of the phosphate on precipitating iron hydroxide.

A study analogous to that reported above for the Fe(III)-PO_4^{-3} reaction was made of the stoichiometry of the Al(III)-PO_4^{-3} reaction. A solution pH of 6.0, that of optimum phosphate removal (see Figures 5, 6, 7, 11, 12, and 13), was used. The data obtained are plotted in Figure 19, 20, and 21. Figure 19 shows phosphate removal as a function of molar ratio. Figure 20 shows residual turbidity and Figure 21 shows residual Al(III) as

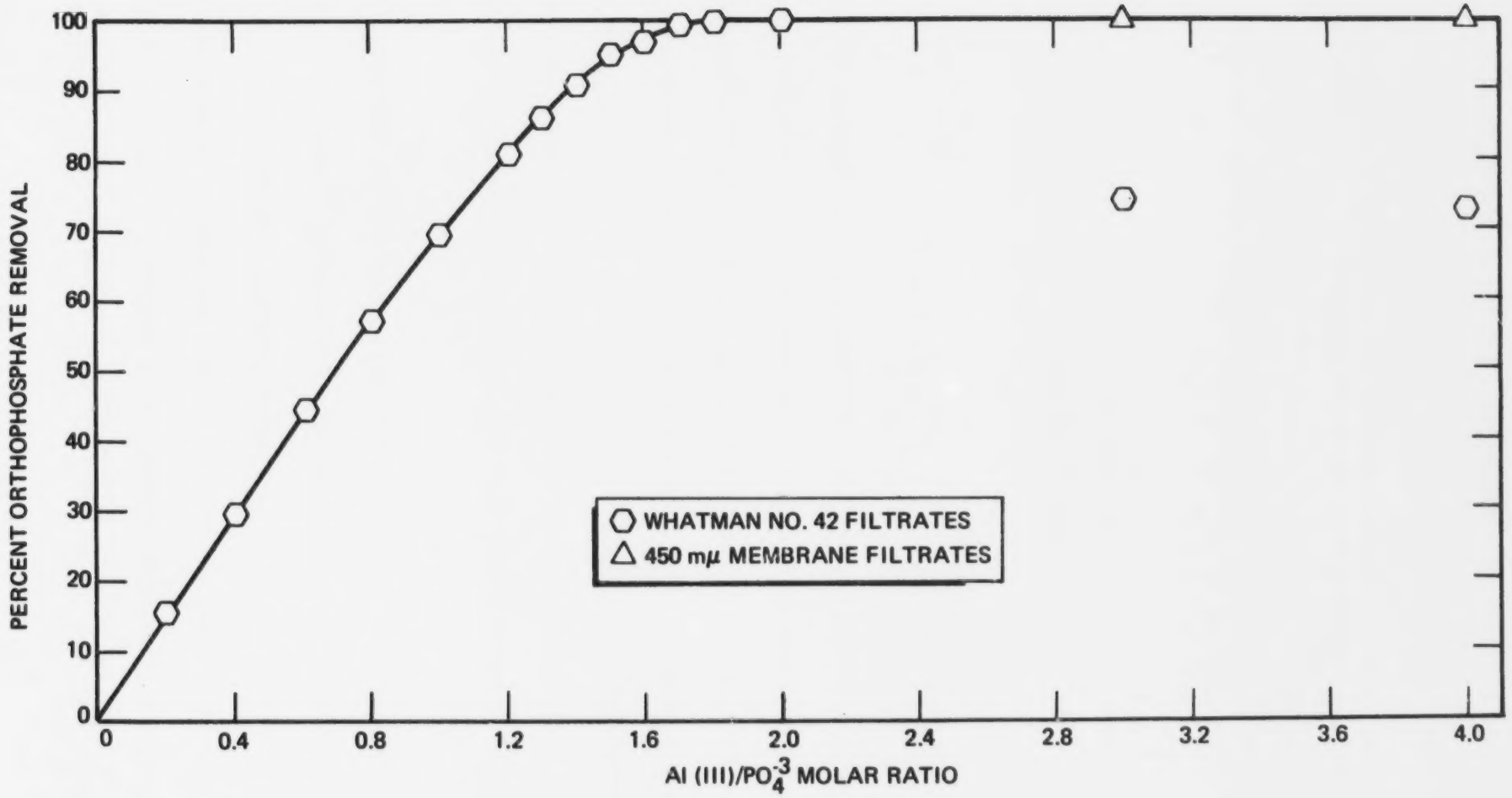

Figure 19. Orthophosphate Removal in Al (III)-Orthophosphate Reaction at pH 6.0 (Initial Orthophosphate Concentration, 12 mg/ℓP)

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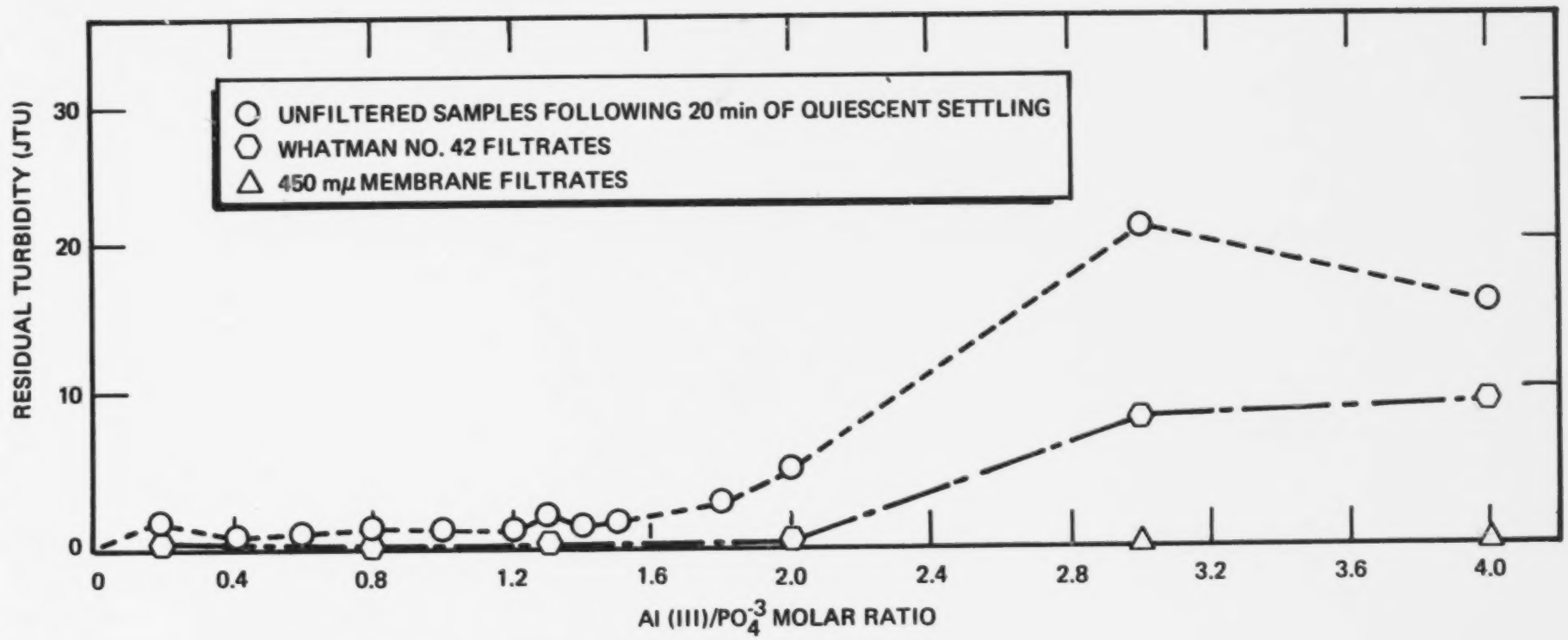

Figure 20. Residual Turbidity in Al (III)-Orthophosphate Reaction at pH 6.0 (Initial Orthophosphate Concentration, 12 mg/ℓ P)

70-A1-032-28

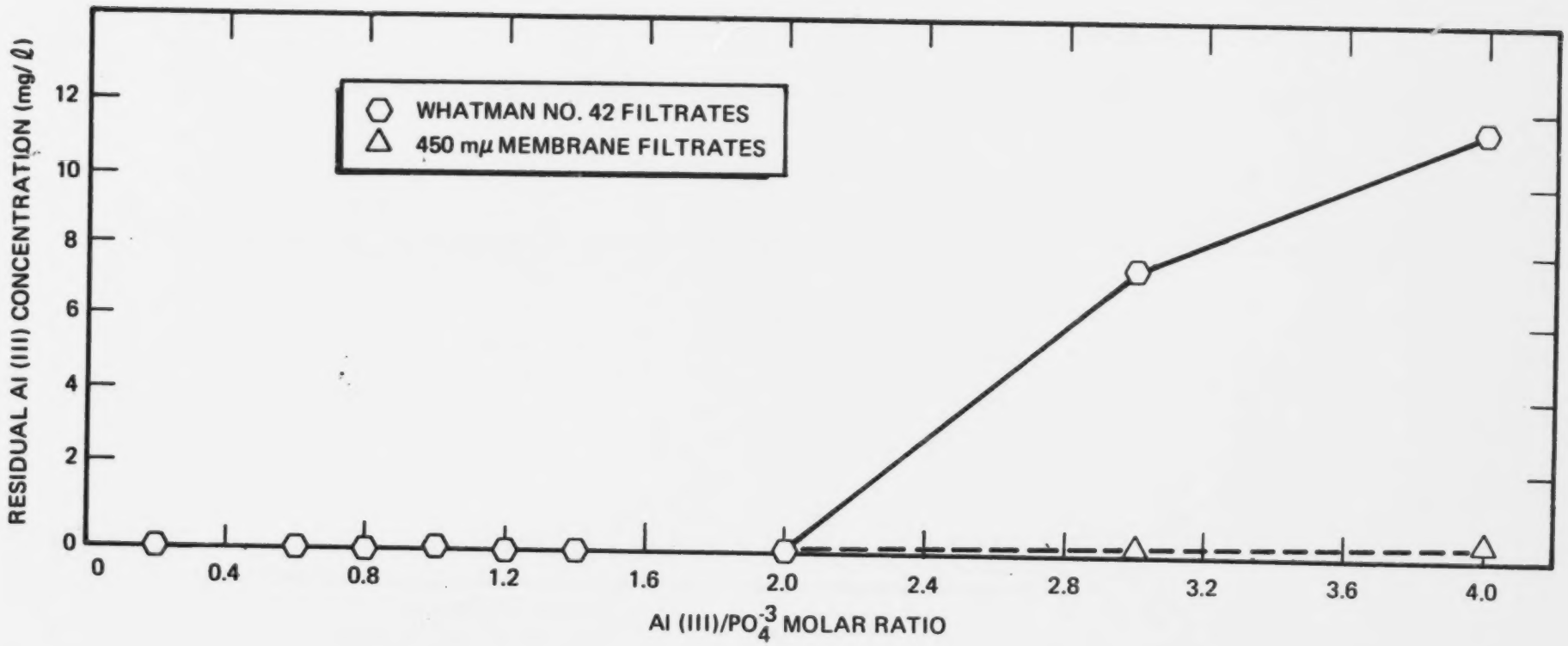

Figure 21. Residual Al (III) in Al (III)-Orthophosphate Reaction at pH 6.0 (Initial Orthophosphate Concentration, 12 mg/ℓ P)

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functions of the molar ratio. In all cases, the values of these parameters at the higher molar ratios may be seen to depend on the fineness of the filter medium used in the analyses.

As with Fe(III), when the pH is kept constant, a direct linear relationship as shown in Figure 19, exists between the amount of added cation and the extent of phosphate removal up to a certain metal-to-phosphate molar ratio (about 1:1 in the case of aluminum-phosphate precipitation at pH 6.0). The existence of such a direct relationship suggests that the reaction between Al(III) and orthophosphate also proceeds on a chemical basis.

It may be seen from the slope of the straight line portion of the phosphate removal curve of Figure 19 that approximately 1.4 mole of Al(III) is required for precipitation of 1 mole of orthophosphate. The corresponding values for Fe(III) at pH 5.0 and 4.0 were 1.23 and 1.22 moles of Fe(III) per mole of phosphate, respectively. This indicates that at the pH levels examined, Al(III) is less effective on a molar basis in precipitating orthophosphate than is Fe(III) and also that, as in the case of Fe(III), hydrolysis products of Al(III) and not the Al^{+3} species alone are involved in the precipitate formation.

When the aluminum-to-phosphate molar ratio was greater than 2.0, the aluminum-orthophosphate reaction, as indicated above, resulted in the formation of fine precipitates which did not settle out very well and could not be completely removed by filtration through Whatman #42 filter paper (see Figures 19, 20, and 21). The colloidal precipitates, however, could be retained on 450 mμ membrane filters. The increased dispersion of these precipitates at high Al(III)/PO_4^{-3} molar ratios is also reflected in a corresponding increase in the concentrations of residual Al(III) and phosphate in

the filtrates obtained by filtration through Whatman #42 paper. In all cases, however, the dispersed colloids could be removed by filtration through 450 mμ membrane filters.

In all studies of the cation-orthophosphate reactions so far described and in the polyphosphate precipitation experiments to be described below, no quantitative assessment was made of the nature and extent of the colloidal surface charge and the role of this surface charge in agglomeration and dispersion of the precipitates. In qualitative terms, it was found that both changes in pH and addition of excess metal cation can result in a dispersion of the phosphate precipitate. The dispersion at higher pH levels may be due to a net negative charge from adsorption of OH^- or of excess PO_4^{-3}. At low pH levels, and also in the presence of excess coagulant, the dispersion of the colloidal precipitates may be due to a positive charge from the adsorption of cations onto the surface of the precipitates. No mobility data were collected in the present study to define regions of charge reversal.

Further Discussion on the Mechanism of Phosphate Removal

Some additional discussion appears in order regarding the question of whether a chemical reaction or adsorption is involved in phosphate precipitation with Fe(III) and Al(III). Lea et al.[4] presented data indicating that the removal of phosphate with Al(III) and Fe(III) salts is accomplished through adsorption rather than by chemical precipitation. Their data, however, do not appear to have been collected under conditions of rigorous pH control necessary to produce consistent results. In regard to the compound formation vs adsorption question, some additional experiments done in the

present study and reported here have shown that freshly precipitated aluminum and iron hydroxides possess very little capacity to precipitate phosphates.

In two jar test experiments, 5 ml of 3.86×10^{-2} M solutions of aluminum and ferric nitrates were added to 495 ml of distilled water and the pH values of the resulting solutions were rapidly (within a period of 2-3 min) raised with NaOH to 6.0 and 5.0, respectively. The subsequent monitoring of pH revealed a small gradual decrease in pH for both solutions, indicating hydrolysis reactions were occurring. The pH of Al(III) solution was 5.67 and 5.51 after 13 and 42 min, respectively; the pH of Fe(III) solution was 4.87 and 4.82 after 4 and 7 min, respectively. While turbidity was developed, no large flocs were formed in either experiment. A second set of experiments was carried out to examine the phosphate removal capacity of these hydrolyzed cations. Following the initial adjustment of pH to 6.0 for Al(III) and 5.0 for Fe(III), 5 ml of 3.86×10^{-2} M Na_2HPO_4 solutions whose pH had been previously adjusted to 6.0 and 5.0 were added to the two metal salt solutions, thereby establishing a 1:1 cation-to-phosphate molar ratio and a phosphate concentration of 12 mg/ℓ P. An immediate (within 5 sec) rise in pH was observed in both cases. The resultant pH of the mixed aluminum-phosphate and ferric phosphate solutions were 6.63 and 6.01, respectively. The initial abrupt rise in the pH was followed by a gradual further increase in pH and after 12 min, the pH of the aluminum and ferric systems were 6.76 and 6.16, respectively. The analysis of the filtrates (100 mμ) from these experiments indicated phosphate residuals of 9.3 mg/ℓ P (for Fe) and 8.4 mg/ℓ P (for Al). Analysis of the Fe(III) solution showed no detectable iron remained in solution. By contrast, residual phosphate

concentrations obtained in phosphate precipitation experiments involving addition of aluminum and ferric salts to a 12 mg/ℓ P phosphate solution (1:1 cation-to-phosphate molar ratio) were between 2 and 3 mg/ℓ P for Fe(III) in the pH 5-6 range and close to 4 mg/ℓ P for Al(III) in the pH 6-7 range. Thus, freshly precipitated aluminum and ferric hydroxide possess little capacity for precipitation of orthophosphate. The rise in the pH observed following addition of phosphate to the aluminum and iron solutions can be attributed to the replacement of hydroxide ions by orthophosphate ions in the precipitates.

Precipitation of Polyphosphates with Al(III) and Fe(III) Salts

The results from the study of the precipitation of pyrophosphate and tripolyphosphates using aluminum and ferric salts (nitrates) are presented in Figures 22-26. The results with pyrophosphate are shown in Figures 22 through 24. Residual phosphate, residual Fe(III), and settled turbidity as a function of pH are shown for a 2:1 equivalence ratio of Fe(III)-to-$P_2O_7^{-4}$ in Figure 22. Figure 23 gives residual phosphate and settled turbidity as functions of pH for an Fe(III)-to-$P_2O_7^{-4}$ equivalence ratio of 1:1. The residual phosphate and settled turbidity for the Al(III)-$P_2O_7^{-4}$ system at a 2:1 equivalence ratio as a function of pH are shown in Figure 24. The residual phosphate and settled turbidity as functions of pH at a 2:1 cation-to-tripolyphosphate ($P_3O_{10}^{-5}$) equivalence ratio are shown for Fe(III) and Al(III) in Figures 25 and 26, respectively.

It may be seen that in all cases the pH ranges for optimum removal of polyphosphates are very narrow. When 2:1 cation-to-phosphate equivalence ratios were used, maximum phosphate removals for both condensed phosphates

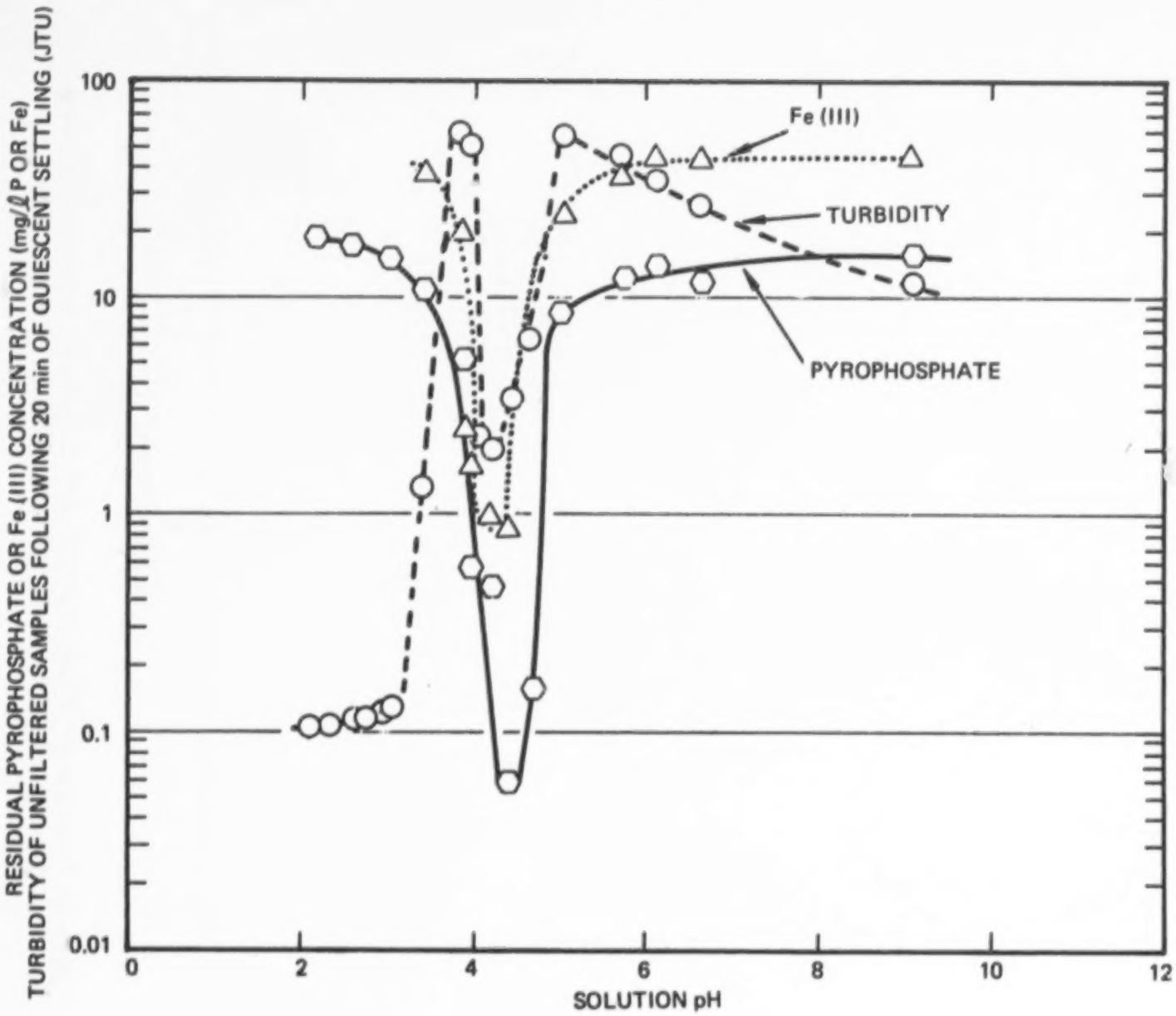

Figure 22. Precipitation of Pyrophosphate with Fe (III) at a 2:1 Cation-to-Pyrophosphate Equivalence Ratio (Initial Pyrophosphate Concentration, 18 mg/ℓ P)

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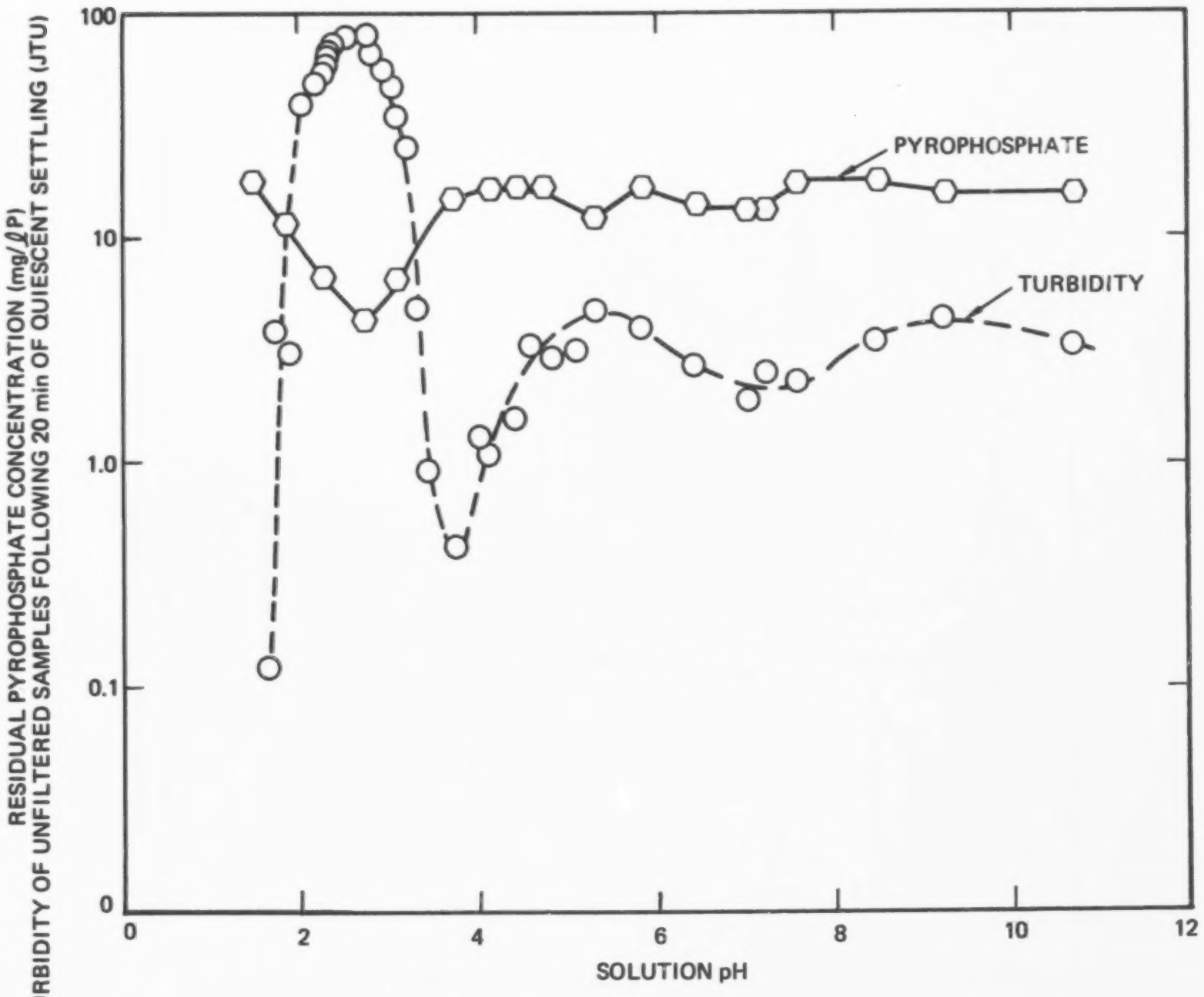

Figure 23. Precipitation of Pyrophosphate with Fe (III) at a 1:1 Cation-to-Pyrophosphate Equivalence Ratio (Initial Pyrophosphate Concentration, 18 mg/ℓP)

70-A1-032-23

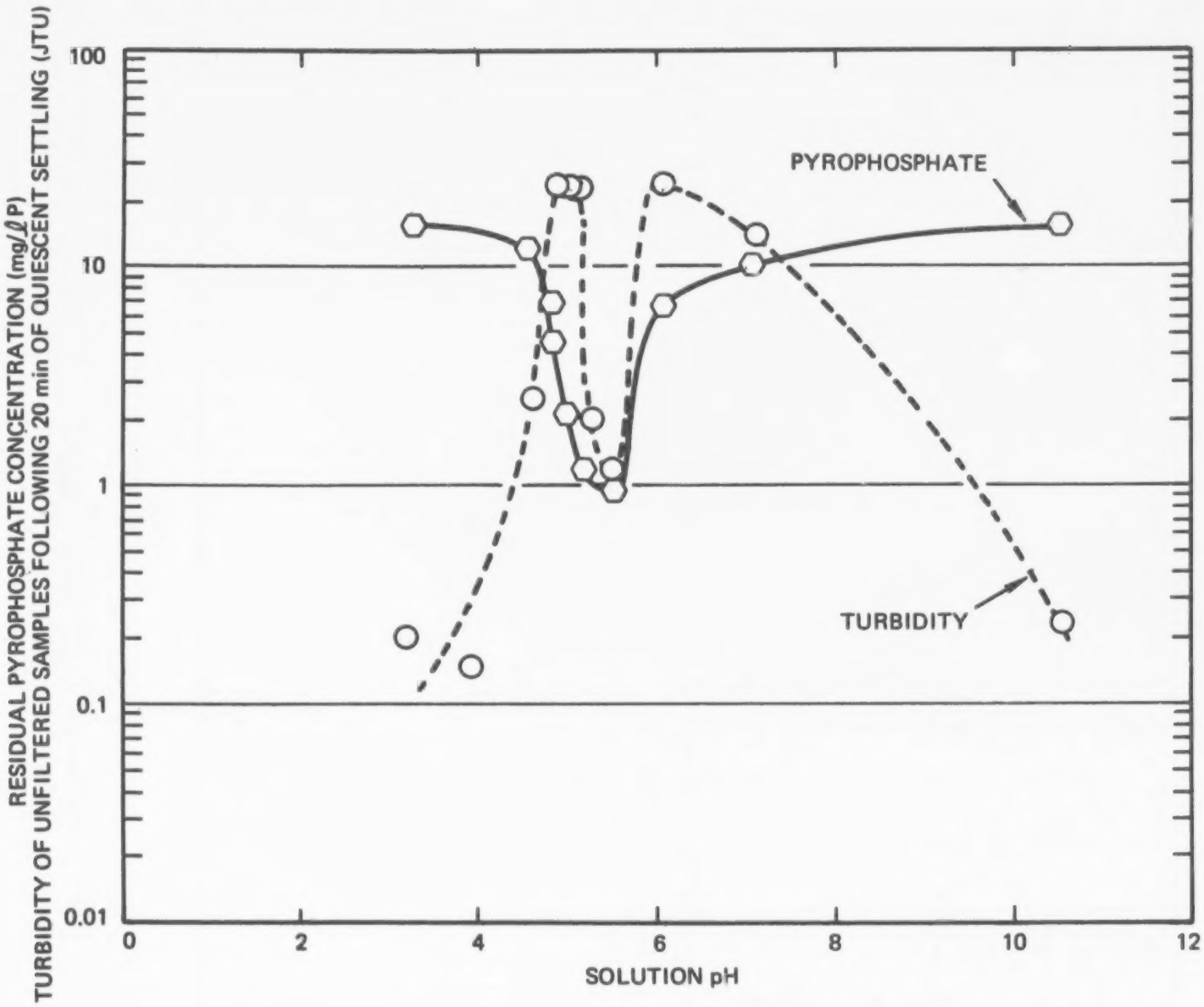

Figure 24. Precipitation of Pyrophosphate with Al (III) at a 2:1 Cation-to-Pyrophosphate Equivalence Ratio (Initial Pyrophosphate Concentration, 18 mg/ℓ P)

70-A1-032-21

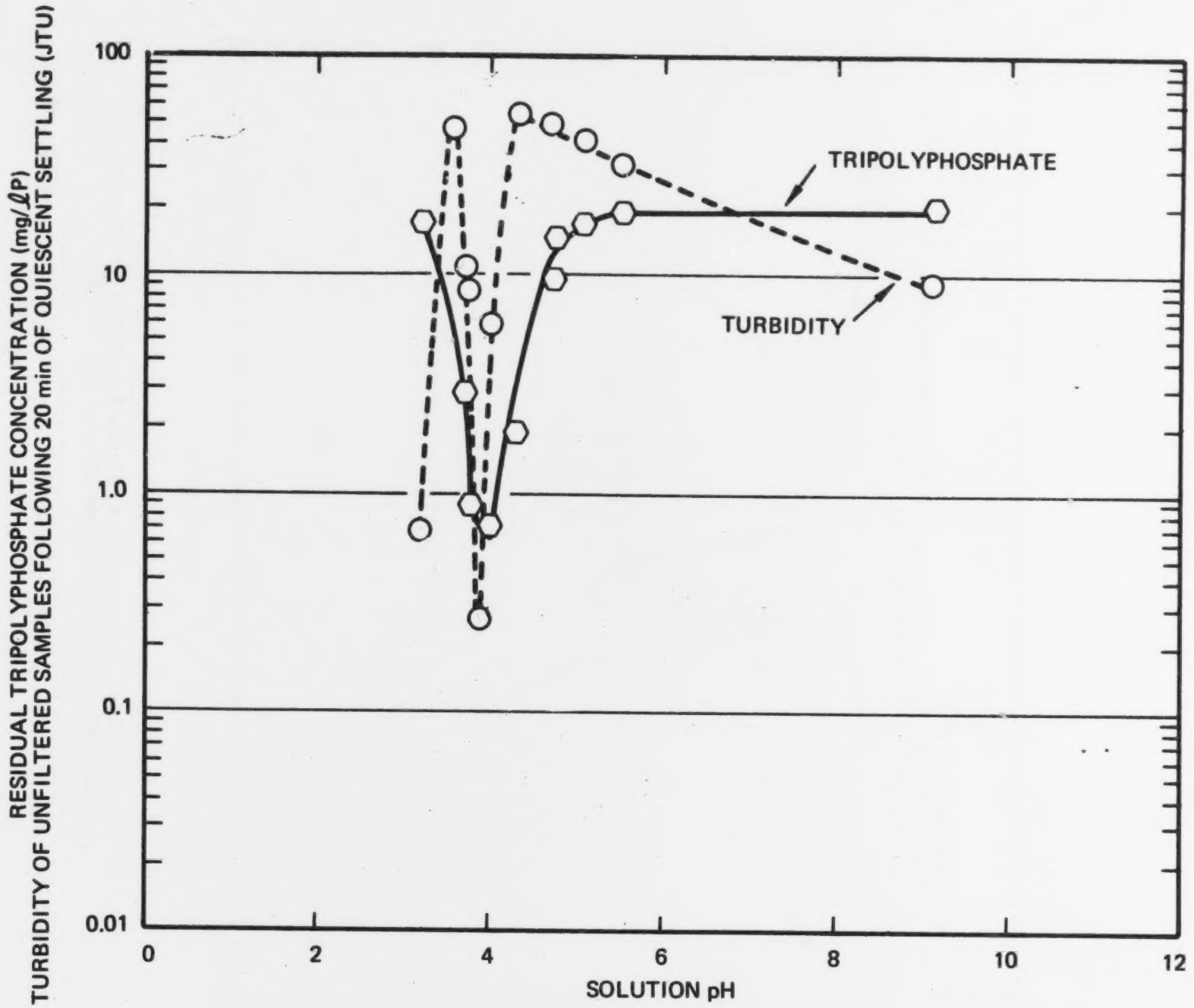

Figure 25. Precipitation of Tripolyphosphate with Fe (III) at a 2;1 Cation-to-Tripolyphosphate Equivalence Ratio (Initial Tripolyphosphate Concentration, 21.6 mg/ℓ P)

70-A1-032-6

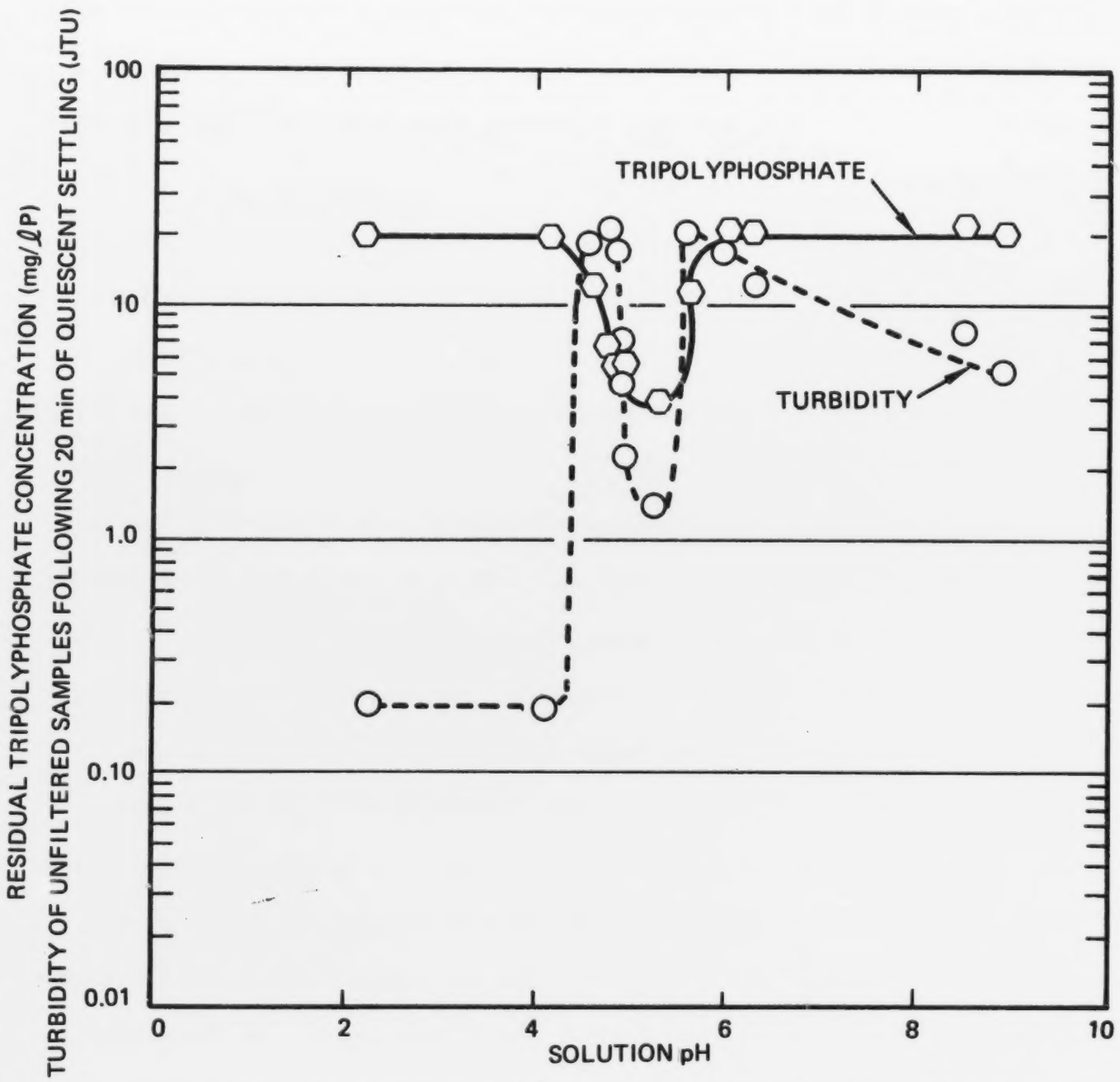

Figure 26. Precipitation of Tripolyphosphate with Al (III) at a 2:1 Cation-to-Tripolyphosphate Equivalence Ratio (Initial Tripolyphosphate Concentration 21.6 mg/ℓ P)

70-A1-032-5

(using Whatman #42 filtration) were observed at pH levels close to 5.5 and 4 for Al(III) and Fe(III), respectively. Practically no phosphate was precipitated at pH levels more than one unit above or below that for maximum removal. Even at 2:1 cation-to-phosphate equivalence ratios and under optimum pH conditions neither Al(III) nor Fe(III) effected complete phosphate removal, although Fe(III) was more effective than Al(III) in that a lower residual phosphate concentration resulted.

Tripolyphosphate was more difficult to precipitate than the pyrophosphate. The minimum tripolyphosphate residual observed was 0.65 mg/ℓ P at pH 4 for Fe(III) and 3.8 mg/ℓ P at 5.3 for Al(III). The corresponding residual pyrophosphate concentrations were 0.055 mg/ℓ P at pH 4.4 for Fe(III) and 0.90 mg/ℓ P at pH 5.5 for Al(III).

At a 1:1 cation-to-tripolyphosphate equivalence ratio, over the pH ranges examined [2.6-8.4 for Al(III) and 3.75-4.15 for Fe(III)], no detectable turbidity developed and no phosphate removal was effected.

It was observed that when a cation-to-phosphate equivalence ratio of 2:1 was used, the cation-polyphosphate reactions at and very near the optimum precipitation pH resulted in the formation of large, settleable flocs; immediately outside this narrow pH range, non-settling turbidity was formed. In the case of Al(III), beyond this pH region no turbidity was observed and no phosphate was removed. Not all the colloidal turbidity was removable by filtration through Whatman #42 filter paper. In the Al(III)-tripolyphosphate case, a significant amount of the residual phosphate was found to be in the colloidal particles which could be removed (probably only partially) by filtration through 100 mμ membrane filters. As indicated in

Table 4, the filtrates from 100 mμ membrane filtration were considerably lower in phosphate content than those obtained by filtration through Whatman #42 filter paper. After filtration through 100 mμ membrane filters, samples 2 and 3 had about the same amount of residual phosphate as that observed at a pH = 5.3 where large settleable flocs were formed and minimum residual phosphate was observed. For this reason and in light of the previous discussion on the cation-orthophosphate reactions, it is conceivable that the apparent narrow pH range of polyphosphate removal may be, at least in part, due to a greater dispersing ability of the polyphosphates relative to orthophosphate. This may also explain why in the pyrophosphate precipitation with Fe(III) at pH levels greater than ~ 5, essentially no removal of iron was effected when the samples were filtered through Whatman #42 filter paper, even though the solutions were turbid (the insoluble iron precipitates remaining in suspension under the dispersing action of the pyrophosphate).

TABLE 4

COMPARISON OF THE TRIPOLYPHOSPHATE CONTENTS OF THE FILTRATES USING 100 mμ MEMBRANE AND WHATMAN #42 FILTER PAPER

(Al(III)-to-Tripolyphosphate Equivalence Ratio = 2:1; Initial Phosphate Concentration = 21.6 mg/ℓ P)

Sample No.	Final Solution pH	Residual Phosphate Content (mg/ℓ P)	
		Whatman #42	100 mμ Membrane Filter
1	4.6	11.9	7.75
2	5.6	12.0	3.75
3	6.0	19.10	4.50

At a 1:1 Fe(III)-to-pyrophosphate equivalence ratio, considerable amounts of turbidity developed in the pH 2-3 range. In this pH range, solutions turned milky after several minutes of slow mixing. The colloidal particles producing the turbidity were fairly stable and did not agglomerate into settleable flocs. The rate of development of turbidity was substantially lower at lower pH levels. At pH = 1.65, for example, the solution remained clear during the experiment, but turned cloudy on standing overnight. As indicated in Figure 23, for this equivalence ratio, the region of maximum turbidity development corresponds to that of maximum phosphate removal. A minimum residual phosphate concentration of 4.5 mg/ℓ P and a maximum turbidity of 80 JTU were observed at pH = 2.75. Although some turbidity developed at nearly all other pH values tested, the removal of phosphate was not appreciable outside the pH 2-3 region at this equivalence ratio.

The behavior of the Fe(III)-pyrophosphate system at the 1:1 ratio, is in sharp contrast to that at the 2:1 ratio (Figure 22). At the 2:1 ratio, no turbidity develops and no phosphate is removed within the pH 2-3 range. Instead, the pH range for maximum phosphate removal lies close to 4.5. Also, the removal of phosphate in this pH range is accompanied by the formation of large flocs which settle out very rapidly.

Phosphate Precipitation Experiments Using Secondary Effluent

The effects of various constituents present in the secondary effluent on the removal of phosphate were collectively evaluated in a series of batch jar tests using effluent from an activated sludge wastewater treatment plant (Tapia Park Treatment Plant, see "Experimental, Materials").

The experiments with Al(III) were conducted as a function of pH using a 2:1 cation-to-phosphate molar ratio. All pH adjustments were made prior to addition of aluminum salt. To estimate the necessary volumes of acid or base which had to be added to the samples to attain a desired range of final pH levels, two samples of the effluent containing the added amount of Al(III) were titrated. The acid titration curve for the secondary effluent-aluminum salt sample is presented in Figure 27.

It should be noted that, to reach the optimum precipitation pH with aluminum, large quantities of acid must be added to the secondary effluent to overcome its natural buffer capacity (see Figure 27). In actual practice, lowering of the pH with the consequent destruction of buffer capacity may be accomplished by addition of acid and/or excess coagulant. The loss of buffer capacity would in itself be undesirable; it would necessitate careful control of chemical addition to avoid wide pH fluctuations. Furthermore, as was demonstrated in the experiments with pure phosphate solutions, the addition of excess coagulant (aluminum or iron salt) can result in the formation of poorly settleable flocs which cannot be effectively removed by plain sedimentation or by ordinary filtration methods.

At pH levels over 8, the addition of NaOH to the effluent prior to addition of aluminum salt resulted in the formation of a precipitate (possibly calcium carbonate and/or calcium phosphate). In these cases, in the actual phosphate removal experiments, the base and the aluminum were added to the sample concurrently. The monitoring of the pH of a sample of secondary effluent treated with Al(III) during the precipitation-flocculation experiment revealed no change in solution pH following an initial

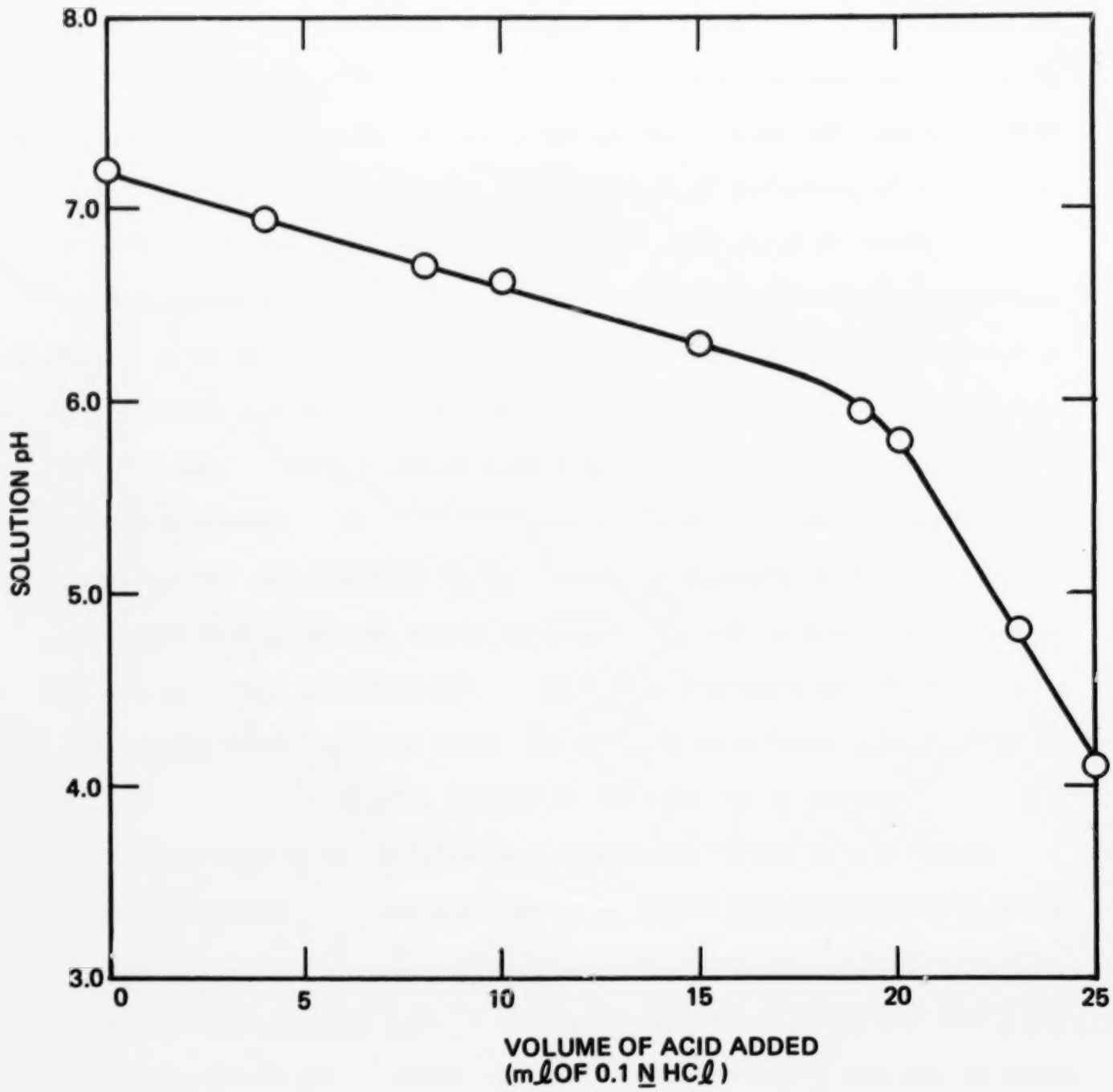

Figure 27. Acid Titration of a Sample of Secondary Effluent 5 x 10^{-4} M in Al (III)

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small drop in pH which took place immediately (less than 10 sec) after the addition of aluminum salt.

The measured residual concentrations of phosphate following precipitation with Al(III) are plotted in Figure 28 as a function of final solution pH. Comparison of the results shown in Figure 28 with those shown in Figure 7 indicates that the removal of phosphate from secondary effluent is similar to the phosphate removal from pure solutions in that in both cases the efficiency of phosphate removal depends on solution pH. As with pure phosphate solutions, the optimum pH for phosphate removal from secondary effluent with aluminum is close to 6. With the secondary effluent, a minimum residual phosphate concentration of 0.04 mg/ℓ P was obtained at this pH of 6.0, whereas the residual phosphate concentrations at all pH levels outside the pH 4.6-6.8 range was more than 0.3 mg/ℓ P.

The stoichiometry of phosphate removal from secondary effluent using ferric nitrate was investigated in a few batch experiments at pH 5.0. The extent of phosphate removal obtained is plotted in Figure 29 as a function of the $Fe(III)/PO_4^{-3}$ molar ratio. As with pure phosphate solutions (Figures 14 and 15) at constant pH, the extent of phosphate removal is directly proportional to the amount of added Fe(III). Comparison of the results shown in Figure 29 with those in Figure 14 indicates that the slope of phosphate removal curve (1.27) is nearly the same for the effluent water as for pure solutions (slope = 1.23). The curve in Figure 29, however, does not pass through the point of origin, thus indicating that a fixed amount of the added iron salt is consumed in reactions with other substances present in the effluent (e.g., organic matter).

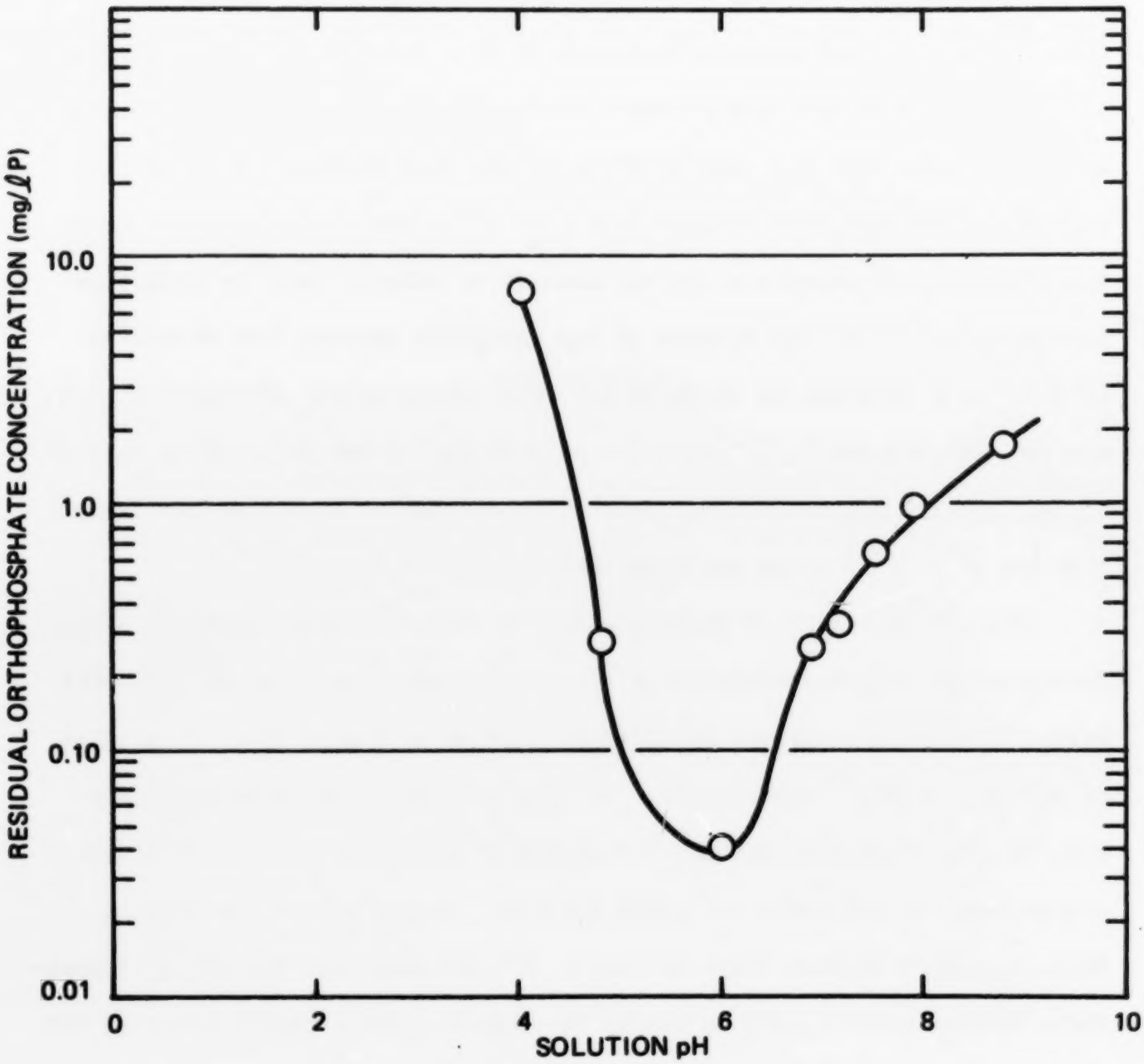

Figure 28. Precipitation of Orthophosphate From Secondary Effluent with Al (III) at a 2:1 Cation-to-Orthophosphate Molar Ratio (Initial Orthophosphate Concentration, 7.75 mg/ℓ P)

70-A1-032-9

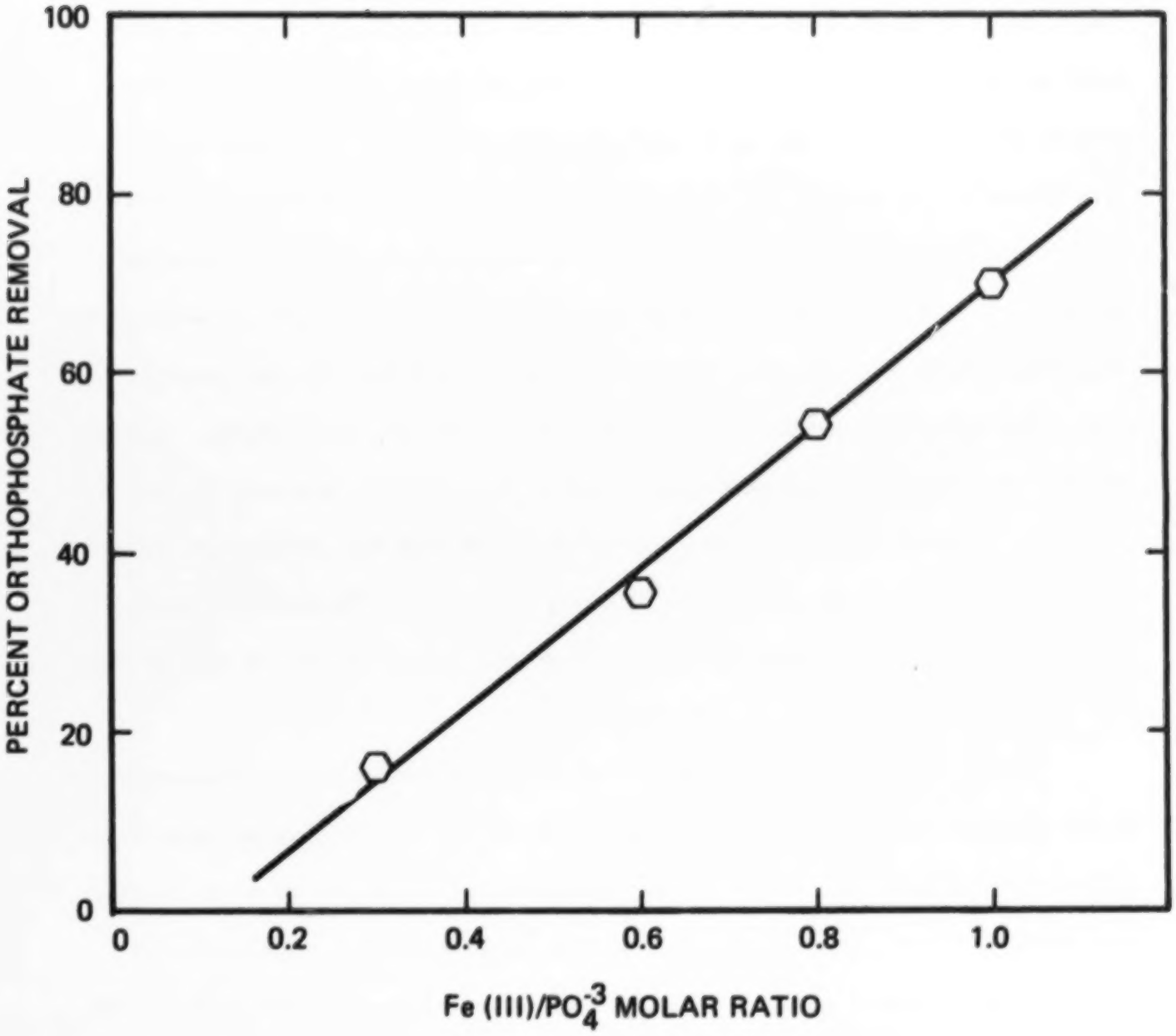

Figure 29. Precipitation of Orthophosphate from Secondary Effluent with Fe (III) at pH 5.0 (Initial Orthophosphate Concentration, 9.0 mg/ℓP)

70-A1-032-7

Nature of the Precipitates Formed in the Reaction of Orthophosphate With Al(III) and Fe(III) Salts

In order to investigate the nature of the precipitates formed by the reaction of orthophosphate ion with Fe(III) and Al(III), reactions were carried out to prepare workable quantities of these precipitates. The method and conditions employed were described above under "Experimental Procedures". As mentioned, the precipitates after collection in Gooch crucibles were kept in a desiccator at room temperature so that a constant weight would be obtained. Neither the aluminum nor the iron phosphate precipitates reached a constant weight even after a 9-day storage period. However, the extent of weight loss after the 7th day was very small. Accordingly, the weight of the precipitate after the 9th day was used in calculating the total water loss at room temperature and the percentage weight loss which resulted in subsequent heating at 104°C. The percent losses in weight at room temperature based on the weight after the first day of drying were about 9.7% for both precipitates.

Weight loss data were obtained on the room temperature desiccator dried samples by heating at 104°C and then at 600°C. Following each heating at temperature for 2 hours, the crucibles were cooled in a desiccator for about 2 hours, weighed, stored in the desiccator for an additional 24 hours and weighed again. Precipitates dried at 104°C were found to be somewhat hygroscopic and slight increases in weight were observed following the first weighing after each heating. Accordingly, the lowest weights observed were used in calculating the weight losses resulting from heating at 104°C. After a portion of the dried precipitates was removed for x-ray

analysis, the remaining precipitate was weighed and ignited at 600°C for two 2-hour periods. Essentially no additional losses in weight were observed following the first 2 hours of ignition.

The aluminum- and iron-orthophosphate precipitates (obtained under the particular precipitation conditions employed) continued to lose weight gradually when heated at 104°C for a total period of six hours. The total weight losses resulting from the 6 hours of heating at 104°C were 7.3 and 9.9% for the iron and aluminum precipitates, respectively, based on the weight dried at room temperature. The corresponding additional weight losses on ignition at 600°C were 8.5 and 12.1%, respectively, based on the weight at 104°C. Correcting for the small portion of the precipitate removed for x-ray analysis, the total percent weight losses on heating at 104°C and then at 600°C are 18.5% and 17.5% for iron and aluminum precipitates, based on the final room temperature weights.

X-ray diffraction analyses were made of the precipitates after drying at room temperature, at 104°C, and after ignition. The precipitates of aluminum and iron dried at room temperature and at 104°C, and the ignited aluminum residue were found to be amorphous under x-ray diffraction examination. The ignited iron residue was found to be crystalline with peaks near those for $FePO_4$. These lines, however, do not correspond exactly, suggesting lattice distortion possibly due to incomplete dehydration.

Cole and Jackson[7] also used thermogravimetric and x-ray diffraction methods to study and characterize the precipitates formed in the reaction of orthophosphate with aluminum and iron. The precipitates they obtained at room temperature were found to be amorphous with x-rays but crystalline

when examined by electron diffraction. They found that extended digestion of the precipitate at 90°C produced a material which gave sharp line x-ray diffraction patterns and had the same electron diffraction patterns as the fresh precipitates. On the basis of this, they concluded that the digestion of the precipitate merely increased crystal size. The species which could be identified in the digested precipitate by x-ray diffraction were variscite, $Al(OH)_2H_2PO_4$, sterrettite, $[Al(OH)_2]_3\ HPO_4\ H_2PO_4$, and strengite, $Fe(OH)_2\ H_2PO_4$. These were assumed then to be also present in the fresh precipitates.

Cole and Jackson[7] also found that the nature of the precipitate is affected by both pH and the rate of precipitation. In the case of Al(III), for example, rapid precipitation and digestion at pH values of 5 to 6 favored the formation of sterrettite while slow precipitation and digestion at lower pH values (2.3-4) favored the formation of variscite. Strengite was found in precipitates obtained with Fe(III) at pH values from 2 to 5.

In addition to these crystallographic data, Cole and Jackson[7] reported that the chemical composition of the precipitated phosphates (determined from ignition losses at 105-800°C and the ratio of the metal-to-phosphate in the precipitate) compared closely with those of the corresponding mineral phosphates. The aluminum-phosphate precipitate obtained at pH 3.8, for example, showed a 21.7% loss on ignition which is close to the 22.8% weight loss calculated for variscite and the 21.6% weight loss calculated for sterrettite. Similarly one precipitate obtained with Fe(III) showed an ignition loss of 20.7% which is close to the 19.3% for strengite.

The procedure followed in the present study differed from that employed by Cole and Jackson, since precipitation was carried out at a single pH, the solution concentrations were lower, and no effort was made to increase the crystal size by digestion or other kinds of treatment. The total losses on heating to 600°C were lower than those reported by Cole and Jackson.[7] As the samples in the present study were dried in a desiccator rather than air dried, there may have been less water content to lose on ignition. Therefore, no direct correlation can be drawn between the results of the present study and that of Cole and Jackson.

RECOMMENDATIONS FOR FUTURE WORK

The basic objectives of the study described in this report have been to clarify certain uncertainties regarding the kinetics and mechanism of phosphate reaction with aluminum and ferric salts. Some of the findings (e.g., the effects of pH, coagulant dose and flocculation time on the efficiency of phosphate removal) are of significant importance from the standpoint of direct application to the large-scale treatment of wastewater for the removal of phosphates. However, it was not the immediate aim of the study to develop criteria to be used by engineers in the design and operation of the necessary treatment units. In fact, except for a few experiments in which actual effluent was used as the phosphate-containing solution, most of the precipitation studies were conducted on pure phosphate solutions. The study of cation-phosphate reaction in pure systems, however, is an essential prerequisite to understanding the phosphate removal process from such complex and variable systems as domestic wastewater. In any application of chemical precipitation methods for the removal of nutrients

from wastewater, the properties of the sludge which is produced are of major engineering concern. In the present study, except for some turbidity data collected on settled solutions following precipitation of phosphate, no effort was made to characterize the precipitates in such engineering terms as the settling rate, resistance to shear, compactibility and dewaterability.

The following areas of research are recommended as a logical extension of the present study:

(1) Evaluation of the effect of certain ionic constituents (e.g., sulfate, calcium, magnesium, carbonate, etc., which are present in wastewater in appreciable concentrations) on the efficiency of phosphate removal.

(2) Determination of the colloidal surface charge (mobility) of the flocs as a function of pH and coagulant dose.

(3) Evaluation of the settling rate and strength (filterability) of the flocs produced in the treatment of various wastewater (settled raw sewage and secondary effluent) with aluminum and iron as a function of pH and coagulant dose.

(4) Investigation of possible means, such as the use of polyelectrolytes, for improving precipitate settleability and filterability.

(5) Characterization of the sludge produced in the treatment of wastewater with aluminum and iron salts. This should include water content, compactibility and dewaterability.

(6) Economic assessment of the large-scale treatment of wastewater using aluminum and iron salts.

SUMMARY

Atomics International has conducted an investigation of the rate, mechanism and stoichiometry of phosphate precipitation with aluminum and ferric salts. Pure solutions of orthophosphate at concentrations representative of those in wastewater, and of pyrophosphate and tripolyphosphate as well as effluent from an activated sludge wastewater treatment plant were used in this investigation. Reaction rate studies were conducted under steady-state conditions of reagent flow in a specially designed reaction kinetics apparatus which permitted rapid mixing of the reactant solutions and subsequent monitoring of pH and residual reactant concentrations of the mixed stream. The effects of pH, reactant concentration, and reagent aging on the efficiency of phosphate removal were evaluated in batch precipitation experiments. The precipitates obtained in the reaction of orthophosphate with aluminum and iron salts under selected conditions were examined by x-ray diffraction, and were characterized by weight loss on heating up to 600°C.

The reaction rate studies showed that the reactions of orthophosphate ion with both Al(III) and Fe(III), which result in the formation of precipitates and the removal of phosphate from solution, are completed in less than 1 sec. No further removal of phosphate is effected following the initial drop in the concentration of soluble phosphate. Lowering of the reaction temperature from ambient to 5°C did not result in any measurable change in the rate or the extent of removal of the phosphate. In all cases examined, the removal of phosphate from solution was accompanied by complete

precipitation of excess Al(III) and Fe(III) by hydrolysis reactions; within the range of sensitivity of the analytical techniques used, these cations could not be detected in the filtered samples.

The removal of orthophosphate was found to be affected by pH, and by the concentration of added aluminum and iron salts. The optimum pH for phosphate precipitation was found to be close to 6.0 for Al(III) and in the vicinity of 3.5-4.0 for Fe(III). For an initial phosphate concentration of 12 mg/ℓ P, the minimum residual phosphate concentrations were 1.85 mg/ℓ P with iron and 3.5 mg/ℓ P with aluminum when a 1:1 cation-to-orthophosphate molar ratio was used. With a 2:1 ratio, minimum phosphate residual concentrations were 0.07 mg/ℓ P and 0.10 mg/ℓ P for iron and aluminum, respectively. At and very near the pH of optimum precipitation, the cation-phosphate reaction resulted in the formation of large, settleable flocs; immediately outside this pH range, colloidal suspensions were formed which in some cases, could be effectively removed only by filtration through 100 mμ membranes. At higher pH levels beyond this pH region, no turbidity was observed with aluminum, but the iron-phosphate solution remained turbid due to the dispersion of ferric hydroxide flocs. No turbidity was formed with either aluminum or iron salts at very low pH levels.

When the pH was kept constant, the removal of orthophosphate with both aluminum and iron salts up to about 1:1 cation-to-phosphate ratio was found to be directly proportional to the concentration of the added cation. The existence of such a direct stoichiometric relationship indicates that a chemical reaction is occurring between the cation and the phosphate and not an adsorption (physical or chemical) of phosphate on the precipitating metal

hydroxide. When phosphate solutions with pH values of 5.0 and 6.0 were added to freshly precipitated colloidal suspensions formed by iron and aluminum salt hydrolysis at the same pH, an immediate sharp rise in pH was observed which was followed by a further small but gradual increase in pH. The rise in the pH is attributed to the replacement of the hydroxides by the phosphate ion in the colloidal particles. In other experiments at a constant pH, it was found that addition of excessive quantities of Al(III) and Fe(III) to a phosphate solution resulted in an impairment of the precipitate settleability and often caused dispersion of the precipitate into extremely fine colloids.

Dilute solutions of Fe(III) (7.72×10^{-4} M; initial pH = 3.0) were found to undergo extensive hydrolysis on aging with a resultant loss of capacity to precipitate phosphate. The behavior of Al(III) in this respect was found to be in sharp contrast to that of Fe(III). No changes in pH, conductivity, or the capacity to precipitate orthophosphate were observed when a 7.72×10^{-4} M solution of Al(III) (initial pH = 4.0) was aged for a period of 2 months.

The removal of condensed phosphates by precipitation with aluminum and iron salts was found to be strongly dependent on pH and the reactant concentration ratio. When a 2:1 cation-to-phosphate equivalence ratio was used with pyrophosphate (initial concentration = 18 mg/ℓ P) and tripolyphosphate (initial concentration = 21.6 mg/ℓ P), maximum removal of phosphate was observed at pH levels close to 4 and 5 with Fe(III) and Al(III), respectively. At this ratio of the reactants, minimum pyrophosphate residual concentrations of 0.9 and 0.06 mg/ℓ P and minimum tripolyphosphate concentrations

of 3.80 and 0.65 mg/ℓ P were observed with Al(III) and Fe(III), respectively. Practically no phosphate was removed at pH levels ± 1 unit from those for maximum removal. At a 1:1 cation-to-phosphate reactant ratio, neither Al(III) nor Fe(III) could effect any removal of tripolyphosphate at several pH levels examined. As with orthophosphate precipitation, good correlations were found between the formation and settleability of the precipitates and the extent of phosphate removal.

The precipitates obtained in the reaction of orthophosphate with aluminum and ferric salts were examined by x-ray diffraction analysis. Both precipitates when dried at room temperature and heated to 104°C, and the aluminum residues after ignition at 600°C, were found to be amorphous. The ferric residue after ignition at 600°C was found to be crystalline with diffraction patterns closely corresponding to those for ferric phosphate. Data were collected on the weight loss which resulted when the desiccator-dried precipitates were heated at 104°C and ignited at 600°C.

REFERENCES

1. Sawyer, C. N., "Some New Aspects of Phosphate in Relation to Lake Fertilization," Sew. and Ind. Wastes, 24, 768 (1952)

2. Finstein, M. S., and Hunter, J. V., "Hydrolysis of Condensed Phosphates During Biological Sewage Treatment," Water Res., 1, 247 (1967)

3. Sawyer, C. N., "Fertilization of Lakes by Agricultural and Urban Drainage," J. N.E. Water Works Assn., 61, 925 (1944)

4. Lea, W. L., Rohlich, G. A., and Katz, W. J., "Removal of Phosphate from Treated Sewage," Sew. and Ind. Wastes, 26, 261 (1954)

5. Henriksen, A., "Laboratory Studies on the Removal of Phosphates from Sewage by the Coagulation Process," Hydrol. J., 24, 1253 (1962)

6. Stumm, W., Discussion in "Advances in Water Pollution Control Research," Proc. 1st Intl. Conf. Water Poll. Res., Pergamon Press Ltd., London, England, Vol. 2, 216 (1964)

7. Cole, C. V., and Jackson, M. L., "Colloidal Dihydroxy Dihydrogen Phosphates of Aluminum and Iron with Crystalline Character Established by Electron and X-ray Diffraction," J. Phys. and Colloid. Chem., 54, 1128 (1950)

8. Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, and FWPCA, 12th ed. (1965)

9. Sandell, E. B., "Colorimetric Determination of Traces of Metals," Interscience Publishers, Inc., N. Y. (1959)

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